Self-Assembly and Nanotechnology Systems

Self-Assembly and Nanotechnology Systems

Design, Characterization, and Applications

Yoon S. Lee

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I had my ear close to her lips.
She whispered, "My son, I missed you so much last night, so, I cried."
Those were the last words my mother left for me.
She was forty-six.
And I am now forty-six.

This is for my mother.

Contents

PREFACE **xvii**

ABBREVIATIONS **xix**

PART I BUILDING UNITS **1**

1 Self-Assembly Systems **3**

1.1. Self-Assembly / 4
1.2. Identification of Building Units / 6
1.2.1. What Is a Self-Assembly Building Unit? / 6
1.2.2. Segmental Analysis / 7
1.2.2.1. Three Fundamental Segments / 7
1.2.2.2. Two Additional Segments / 11
1.3. Implication of Building Unit Structures for Self-Assemblies / 15
1.4. General Assembly Diagram / 17
1.5. Collection of Building Units / 23
1.5.1. Basic Building Units / 23
1.5.2. Directionally Assembling Building Units / 26
1.5.3. Asymmetrically Packing Building Units / 28
1.5.4. Functional Building Units / 28
1.6. Concluding Remarks / 30
References / 31

2 Nanotechnology Systems **33**

2.1. Nanoassembly / 35
2.2. Identification of Building Units / 37
2.2.1. What Is a Nanoassembly Building Unit? / 37
2.2.2. Fabrication Building Units / 38
2.2.3. Reactive Building Units / 40
2.3. Nanoelements / 41
2.4. Implication of Building Unit Structures for Nanoassemblies / 42
2.5. General Assembly Diagram / 45
2.6. Self-Assembly, Nanoassembly, and Nanofabrication / 51
2.7. Collection of Building Units / 54
2.7.1. Ligand-Protected Nanoparticles / 54
2.7.2. Functional Surfaces / 56
2.7.3. Reactive Precursors / 57
2.7.4. Substrates / 57
2.7.5. Reducing Agents / 58
2.8. Concluding Remarks / 58
References / 60

PART II DESIGN **61**

3 Identification of Self-Assembly Capability **63**

3.1. Assembly Issue / 63
3.2. General Overview / 64
3.3. Assembly Principles / 65
3.3.1. Molecular Self-Assembly / 65
3.3.1.1. Ionic Surfactants / 69
3.3.1.2. Nonionic Surfactants / 70
3.3.2. Colloidal Self-Assembly / 71
3.3.2.1. Colloids with Different Origins / 74
3.3.2.2. Colloids with Different Sizes / 75
3.3.3. Directionally Assembling Systems / 77
3.3.4. Self-Assembly at Surfaces / 81
3.3.4.1. Hydrophobic Surfaces / 82
3.3.4.2. Hydrophilic Surfaces / 87
3.4. Collection of Primary Self-Assembled Aggregates / 89
3.5. Summary / 89
References / 91

4 Identification of Multi-Step Self-Assemblies 93

4.1. Assembly Issue / 93
4.2. General Overview / 94
4.3. Assembly Principles / 96
4.3.1. Molecular Self-Assembly of Surfactants / 97
4.3.2. Colloidal Self-Assembly / 102
4.4. Collection of Higher-Order Self-Assembled Aggregates / 105
4.5. Collection of Self-Assembled Aggregates within Biological Systems / 107
4.6. Summary / 108
References / 110

5 Control of the Structures of Self-Assembled Aggregates 111

5.1. Assembly Issue / 111
5.2. General Overview / 112
5.2.1. Primary Self-Assembled Aggregates / 112
5.2.2. Higher-Order Self-Assembled Aggregates / 113
5.3. Assembly Principles / 115
5.3.1. Primary Self-Assembled Aggregates / 115
5.3.1.1. Molecular Systems I / 117
5.3.1.2. Molecular Systems II / 121
5.3.1.3. Colloidal Systems / 125
5.3.2. Higher-Order Self-Assembled Aggregates / 130
5.3.2.1. Molecular Systems / 132
5.3.2.2. Colloidal Systems / 134
5.4. Collection of the Structures of Self-Assembled Aggregates / 136
5.4.1. Primary Self-Assembled Aggregates / 136
5.4.2. Higher-Order Self-Assembled Aggregates / 137
5.5. Summary / 139
References / 140

6 Hierarchy and Chirality of Self-Assembled Aggregates 141

6.1. Assembly Issue / 141
6.2. General Overview / 142
6.3. Assembly Principles / 143
6.3.1. Molecular Systems / 145
6.3.2. Surface Systems / 148
6.4. Collection of Hierarchy within Self-Assembled Aggregates / 156

6.5. Collection of Chirality Expressed by Self-Assembled Aggregates / 157
6.6. Summary / 159
References / 160

7 Assembly with Multiple Building Units 161

7.1. Assembly Issue / 161
7.2. General Overview / 163
7.3. Assembly Principles / 164
7.3.1. Analysis of Building Units / 164
7.3.2. Assembly of Nanoassembled Systems / 168
7.3.2.1. Homogeneous Assemblies / 168
7.3.2.2. Sequential Assemblies / 172
7.3.2.3. Hierarchical Assemblies / 177
7.3.3. General Assembly Trends / 180
7.3.3.1. Homogeneous Assemblies / 180
7.3.3.2. Heterogeneous Assemblies I / 182
7.3.3.3. Surface Assemblies / 183
7.3.3.4. Heterogeneous Assemblies II / 184
7.4. Collection of Nanoassembled Systems I / 185
7.5. Collection of Nanoporous Solids / 186
7.5.1. Synthetic Zeolites / 187
7.5.2. Metal-Organic Frameworks / 189
7.6. Summary / 189
References / 189

8 Directed and Forced Assemblies 191

8.1. Assembly Issue / 191
8.2. General Overview / 192
8.3. Assembly Principles / 196
8.3.1. Analysis of Building Units / 196
8.3.2. Assembly under External Forces / 199
8.3.2.1. Forced Assemblies / 199
8.3.2.2. Directed/Forced Assemblies / 204
8.3.2.3. Directed Assemblies / 208
8.3.3. General Assembly Trends under External Forces / 213
8.3.3.1. Forced Assemblies / 214
8.3.3.2. Directed/Forced Assemblies / 215
8.3.3.3. Directed Assemblies / 216

8.3.3.4. Window of Critical External Forces / 218
8.4. Techniques for Directed and Forced Assemblies / 219
8.5. Surface-Induced Directed and Forced Assemblies / 220
8.6. Collection of Nanoassembled Systems II / 220
8.7. Summary / 222
References / 222

PART III APPLICATIONS 225

9 External Signal–Responsive Nanomaterials 227

9.1. Nanoissue / 227
9.2. General Overview / 228
9.3. Assembly Principles / 231
9.3.1. External Signal–Responsive Molecular Assemblies / 231
9.3.1.1. Light-Responsive Assemblies / 232
9.3.1.2. Catalytic Reaction–Responsive Assemblies / 235
9.3.1.3. Electrochemical-Responsive Assemblies / 237
9.3.1.4. Solution pH–Responsive Assemblies / 239
9.3.2. External Signal–Responsive Colloidal Assemblies / 242
9.3.2.1. Thermo-Responsive Assemblies / 244
9.3.2.2. Solution pH–Responsive Assemblies / 245
9.3.2.3. Magnetic Field–Responsive Assemblies / 247
9.4. Collection of External Signal–Responsive Assembly Systems / 250
9.5. From Assembly Systems to Nanomaterials / 250
9.6. Collection of External Signal–Responsive Nanomaterials / 253
9.7. Summary / 254
References / 255

10 Nanomaterials with Intrinsic Functionalities 257

10.1. Nanoissue / 257
10.2. General Overview / 258
10.3. Assembly Principles / 261
10.3.1. Molecular Assembled Systems / 263
10.3.2. Colloidal Assembled Systems / 267
10.4. From Assembled Systems to Nanomaterials / 270
10.5. Collection of Nanomaterials with Intrinsic Functionalities / 270
10.6. Summary / 272
References / 272

11 Nanostructures: Designed to Perform 275

11.1. Nanoissue / 275
11.2. General Overview / 276
11.3. Assembly Principles / 277
11.3.1. Analysis of Building Units / 277
11.3.2. Nanostructure Assemblies / 281
11.3.3. Nanopore-Based Nanostructures / 283
11.3.4. Nanoparticle-Based Nanostructures / 287
11.3.5. Nanofilm-Based Nanostructures / 292
11.3.6. General Trends / 297
11.4. Collection of Common Nanostructure Names / 298
11.5. Collection of Nanostructures and Their Applications / 298
11.6. Summary / 301
References / 303

12 Nanoproperties: Controlled to Express 305

12.1. Nanoissue / 305
12.2. General Overview / 306
12.3. Assembly Principles / 307
12.3.1. Analysis of Building Units / 307
12.3.2. Different Types of Nanoproperties / 313
12.3.3. Assemblies to Obtain Nanoproperties / 316
12.3.4. Individual Types of Nanoproperties / 318
12.3.5. Collective Types of Nanoproperties / 321
12.3.6. Cooperative Types of Nanoproperties / 324
12.3.7. General Trends / 327
12.4. Collection of Nanoproperties and Their Applications / 328
12.5. Summary / 329
References / 331

13 Nanofabricated Systems: Combined to Function 333

13.1. Nanoissue / 333
13.2. General Overview / 334
13.3. Fabrication Principles / 335
13.3.1. Analysis of Building Units / 336
13.3.2. Nanofabrication / 340
13.3.3. Bottom-Up Approach / 342
13.3.4. Top-Down Approach / 345

13.3.5. Bottom-Up/Top-Down Hybrid Approach / 347
13.3.6. General Trends / 350
13.4. Collection of Top-Down Techniques / 352
13.5. Collection of Top-Down Bulk Materials and Functionalizing Agents / 352
13.6. Collection of Nanofabricated Systems and Their Applications / 353
13.7. Summary / 353
References / 356

14 Nanomechanical Movements: Combined to Operate 359

14.1. Nanoissue / 359
14.2. General Overview / 360
14.3. Fabrication Principles / 361
14.3.1. Element Motions / 361
14.3.2. Working Mechanisms / 362
14.3.3. Analysis of Building Units / 364
14.3.4. Periodic Push Motions / 372
14.3.5. Periodic Pull Motions / 374
14.3.6. Push–Pull Motion Cycles / 375
14.3.7. Periodic Push Motions under Guide Motion / 378
14.3.8. Periodic Pull Motions under Guide Motion / 380
14.3.9. Push–Pull Motion Cycles under Guide Motion / 383
14.3.10. General Trends / 385
14.4. Collection of Nanomechanical Movements / 386
14.5. Summary / 390
References / 390

PART IV CHARACTERIZATION 393

15 Assembly Forces and Measurements 395

15.1. Intermolecular and Colloidal Forces / 395
15.2. Collection of Intermolecular and Colloidal Forces / 396
15.3. Measurements of Intermolecular and Colloidal Forces / 396
15.3.1. Atomic Force Microscopy / 396
15.3.2. Surface Forces Apparatus / 398
15.4. Collection of Measurement Techniques / 399
15.5. Implications of Building Unit Structures for Characterization / 399
References / 402

16 Assembly Processes and Critical Behaviors 405

16.1. Critical Behaviors as the Characterization Guide of Assembly Processes / 405
16.2. Characterization Principles / 407
16.2.1. Self-Assembly Capability / 407
16.2.1.1. Molecular Systems / 407
16.2.1.2. Colloidal Systems / 409
16.2.2. Multi-Step Self-Assemblies / 410
16.2.2.1. Molecular Systems / 410
16.2.2.2. Colloidal Systems / 412
16.3. Collection of Physical Properties to Measure / 413
16.4. Collection of Critical Assembly Parameters / 414
References / 414

17 Assembled Systems and Structural Properties 417

17.1. Structural Properties for the Characterization of Assembled Systems / 417
17.2. Characterization Principles / 419
17.2.1. Structures of Primary Assembled Systems / 419
17.2.1.1. Molecular Systems / 419
17.2.1.2. Colloidal Systems / 421
17.2.2. Structures of Higher-Order Assembled Systems / 422
17.2.3. Hierarchy and Chirality / 422
17.2.4. Effect of External Forces / 425
17.2.5. Functional Assembled Systems / 426
17.3. Collection of Structural Properties to Measure / 427
References / 427

18 Modeling and Simulations 429

18.1. Assembly Systems Are Big and Multi-Scaled / 429
18.2. Classic Models / 430
18.2.1. Thermodynamic Models / 430
18.2.2. Colloidal Model / 430
18.2.3. Geometrical Model / 431
18.2.4. Elastic Model / 431
18.2.5. Isotherms / 431
18.3. Simulations / 431
18.3.1. Electronic Simulations / 432
18.3.1.1. Density Functional Theory / 432

18.3.1.2. Mean-Field Theory / 433
18.3.2. Atomistic Simulations / 433
18.3.2.1. Molecular Dynamics and Monte Carlo Methods / 433
18.3.3. Coarse-Grained Simulations / 433
18.3.3.1. Dissipative Particle Dynamics / 434
18.3.3.2. Patchy Particle Model / 434
18.3.3.3. Brownian Dynamics / 435
18.3.3.4. BRAHMS / 435
18.3.3.5. MARTINI / 436
18.3.4. Continuum Simulations / 436
18.3.5. Multi-Scale Simulations / 436
18.4. Concluding Remarks / 437
References / 437

EPILOGUE

Informatics for Self-Assembly and Nanotechnology Systems **441**

E.1. Background / 441
E.2. Definition and Principle / 443
E.3. Structure / 444
E.4. Development and Benefits / 445
E.5. Challenges / 446
References / 446

INDEX **449**

Preface

Nanotechnology is now experiencing a nice expansion toward its full potential. Early promises from scientific discoveries are being actualized in engineering stages, and diverse products are beginning to show up in the marketplace. This is possible because we now have some good methods for the assembly of nanotechnology systems and an improved understanding of how they behave at the nanoscale.

Self-assembly is a key scientific principle behind nanotechnology. Many of the seemingly complex self-assembly systems from different origins are well understood. They can help assemble nanotechnology systems effectively and efficiently, and provide practical tools to control the structures and properties of nanotechnology systems. This marriage of self-assembly and nanotechnology systems is important for the maturation of nanotechnology and promises fruitful outcomes. A main goal of this book is to offer comprehensive coverage of how to use self-assembly systems for the design, characterization, and applications of nanotechnology systems. The four key objectives are:

1. Show how to identify assembly building units.
2. Provide detailed assembly principles for the design of nanotechnology systems.
3. Establish practical assembly methods to focus on when developing nanomaterials, nanostructures, nanoproperties, nanofabricated systems, and nanomechanics.
4. Show how to characterize/model self-assembly and nanotechnology systems.

This book is divided into four parts. The first part shows the assembly building units, and how diverse their origins and structures can be. It also presents how

to analyze the building unit structures in a systematic manner. This will be called *segmental analysis*, which is used as an underlying concept for the discussions throughout the book. The second and third parts show the design and applications of nanotechnology systems, respectively, and how to select proper assembly principles and methods. The last part shows how to select proper characterization techniques and predictive models. This book is structured as follows:

1. Clear questions at the beginning of each chapter help readers stay focused.
2. Each chapter offers an algorithmic diagram for a general overview.
3. Schematics are designed to link the assembly principles with actual systems.
4. Case studies are provided for the in-depth analysis of actual systems.
5. All chapters (except for the final one) provide a collection of examples.
6. All chapters in the second and third parts follow the same format, making it easy to understand different assembly principles and methods.

Those who are studying the disciplines of science and engineering with a general chemistry level of knowledge should not have too much difficulty using this book. Occasional trips to common biology, physics, or materials science textbooks might be necessary. This book will be useful for:

1. Students, researchers, and professionals who want to acquire a general picture of how self-assembly systems are used in nanotechnology systems.
2. College teachers who need a convenient source for teaching and for design of experiments for nanotechnology-related courses.
3. Nanoscientists and nanotechnologists who need a handbook for their daily activities and for publishing the results of their studies.

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I am deeply grateful to all the reviewers. Their valuable advice greatly helped me shape this book. I can never thank enough professors Kyu Whan Woo at Seoul National University and James F. Rathman at Ohio State University. It was Professor Woo who introduced me the term *self-assembly* on my first day of graduate school. This word has been imprinted on my mind ever since. With the guidance of Professor Rathman, I widened my view on self-assembly and explored a good deal of nanotechnology. My deep thanks extend to Dr. Oksik Lee at Chemical Abstracts Service. Without her companionship, thoughtfulness, and all the discussions I have had with her over the years, it would have been much more difficult to write this book. As always, my deepest thanks go to my wife, Jee-a, and my son, Jong-hyeok, for their endless support and love. I always miss my parents and my parents-in-law, who live far away.

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Abbreviations

The following abbreviations are used in the figures and tables. Full terms are used in the text.

attractive segment: **A**
repulsive segment: **R**
directional segment: **D**
asymmetric packing segment: **AP**
external force-specific functional segment: **EF-F**

attractive force: **AF**
repulsive force: **RF**
directional force: **DF**
asymmetric packing process: **APP**
external force-induced directional factor: **ED**

self-assembly: **SA**
self-assembled aggregate: **SAA**
self-assembly building unit (primary): **SA-BU**
primary self-assembly process: **P-SA**
primary self-assembled aggregate: **P-SAA**
secondary self-assembly building unit: **S-SA-BU**
secondary self-assembly process: **S-SA**
secondary self-assembled aggregate: **S-SAA**

tertiary self-assembly building unit: **T-SA-BU**
tertiary self-assembly process: **T-SA**
tertiary self-assembled aggregate: **T-SAA**

nanoassembly: **NA**
nanoassembled system: **NA-S**
nanoassembly building unit: **NA-BU**
fabrication building unit: **F-BU**
reactive building unit: **R-BU**
nanostructural element: **N-SE**
nanoproperty element: **N-PE**
nanomechanical element: **N-ME**
nanocommunication element: **N-CE**

nanofabrication: **NF**
nanofabricated system: **NF-S**
nanointegrated system: **NI-S**
nanodevice: **NaD**
nanomachine: **NaM**

Part I

Building Units

1

Self-Assembly Systems

My ten-year-old son loves building action figures using LEGO bricks (LEGO, please see References). He has many LEGO products, "which I bought for him, of course." He first built the action figures that he was supposed to build by following the instructions. Once he built enough number of them in many different forms, he then began to build his own action figures by using the parts from the different boxes. Whenever I am watching him building new forms of action figures, in many cases with new functions, I am amazed by how an "unbiased" child's mind can do such a creative and fun thing. I love watching him doing that, and, of course, enjoy the new action figures so much. What is also amazing is the flexibility of those tiny parts. They are small and simple but at the same time so elegantly and functionally designed. It seems to me that their core structures are composed of just a couple of different basic segments. These basic segments are simple yet diverse, and easy to assemble. One segment from one part perfectly fits with the complementary segments from all other parts even from other types of action figures. By following this simple rule, my son keeps building his own action figures with a high variety and different size scales.

My approach to self-assembly begins with the segmental analysis of self-assembly building units. (The term *building block* is used roughly ten times more than the term *building unit* in the literature. But the term *building block* may bring an unintended implication that it is limited to sizable materials rather than encompassing a wide range of different entities. Thus, the term *building unit* will be used in this book with the intention that it includes any type of entity that can be assembled into any type of self-assembled system.) It does not totally

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come from my son's LEGO playing, but it has definitely helped me build up this concept. It is not about making self-assembly analysis more complicated. There is a very simple way to address self-assembly issues that are seemingly widely dispersed. And we can benefit from it, not just in nanotechnology but in other areas of modern technology as well. It may not look like a conventional scientific approach toward natural phenomena. But it is indeed possible to understand self-assembly with a very simple rule.

1.1. SELF-ASSEMBLY

Figure 1-1 presents a schematic explanation of the self-assembly process based on the concept of *force balance*. A full description of this concept has been discussed elsewhere (Lee, 2008). For almost all of the self-assembly processes, major interactions between their building units, regardless of the types and sizes, occur through relatively weak intermolecular or colloidal forces. These include hydrogen bond, van der Waals interaction, hydrophobic force, π-π interaction, steric interaction, depletion force, solvation/hydration forces, and so forth. Strong bonds such as covalent bond, coordination bond, or ionic bond are rarely involved with self-assembly processes. These weak intermolecular or colloidal forces can be classified into three distinctive groups whose delicate balance determines the process and outcome of the self-assembly. They are attractive driving force, repulsive opposition force, and directional/functional forces. The attractive driving force acts to bring self-assembly building units together, thus initiating the self-assembly process. Once this attractive process takes place, the repulsive opposition force, which is originated by another segment within the self-assembly building unit, acts to balance the attractive process, which places the building units at a certain critical state. Self-assembly is established at this critical point and self-assembled aggregates begin to appear at this point as well. The third group, directional/functional forces,

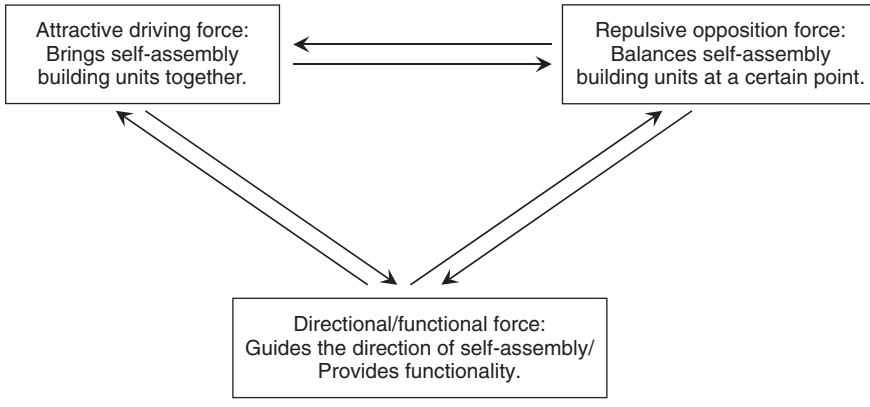

Figure 1-1. The concept of force balance approach for self-assembly.

are the forces that can guide this balancing process between the attractive and repulsive forces. Depending on the nature of the self-assembly system, the directional/functional forces can act as either an attractive force or a repulsive force. In most cases, it is the directional/functional forces that give the self-assembly system (or self-assembled aggregate) unique structural functionalities.

Self-assembly occurs through the delicate balance between at least any two groups of the forces. For example, it can be between the attractive force and repulsive force, between the attractive force and the directional force that has the capability of the repulsive force, between the repulsive force and the directional forces that have the capability of the attractive force, or between all three groups. But, to become a self-assembly, it always has to fulfill both the "self" aspect and the "assembly" aspect, and at the same time should have the actual outcomes, that is, "self-assembled aggregates." Therefore, there always has to be the force that gives the "self" aspect to the self-assembly building units and the balance that can ensure both the structural integrity and dynamic flexibility of the self-assembled aggregates. On the other hand, this observation leads us to the justification that, once the conditions (intrinsic ones of the building unit and environmental ones) for this force balance are met between any building units, they will come close ("self" aspect) and form the aggregates (self-assembled aggregates) at a certain point of the process ("assembly" aspect) regardless of their types and sizes.

Certainly, the conditions that can induce thermodynamic equilibrium between the self-assembly building units at the balance point will ensure the self-assembly process. *Equilibration process* means bringing the building units together ("self" aspect), and *equilibrium state* means holding the self-assembled aggregates flexible yet with structural integrity ("assembly" aspect). However, there can be kinetic conditions that can also ensure the two aspects of the self-assembly processes and self-assembled aggregates. There can be a certain point (or points) during any types of kinetic processes where the building units can be close ("self" aspect) and maintain the state until they escape from the point ("assembly" aspect). This leads to the conclusion that self-assembly processes do not always have to be driven thermodynamically. They can also be driven by kinetic processes. Self-assembled aggregates can maintain their structural integrity and ensure dynamic flexibility not just by keeping them at equilibrium state but by a kinetically stable "force well" also.

Figure 1-2 shows an arbitrary energy profile between self-assembly building units as a function of their coordination of assembly. The interaction energy (or force) between building units is varied as the distance between them (coordination) is changed. The profile can have just monotonic characteristics if it is assumed that the interaction is through only attractive or repulsive force. However, they can also go through somewhat complicated patterns of profile curves as shown in the figure. This will be more realistic in cases where the structures of self-assembly building units become more diverse. Also, when the self-assembly is induced by external environmental conditions, the energy profile can be a lot more complicated. Points a and b in the figure are the points where the self-assembly building units come close together and maintain the structural integrity of their self-assembled

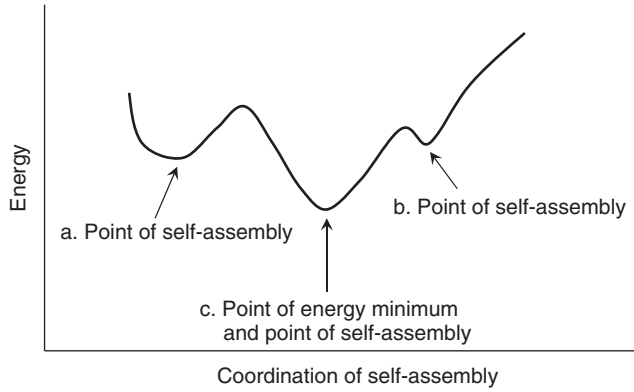

Figure 1-2. The concept of force balance can embrace a wider scope of self-assembly than the energy minimization approach.

aggregates. This will be the case until they are preceded further into the process by following their kinetic nature or as long as energy is being supplied into the system to maintain their state. Therefore, both a and b are the points of self-assembly driven by kinetic process. This is called a *dynamic self-assembly*. Point c in the figure is the point of energy minimum, that is, the point of equilibrium. The self-assembly building units are being brought into this point by their equilibration process and maintain their equilibrium state. This is called a *static self-assembly*. For more details about these two classes of self-assembly and some additional argument, please refer to Rouvray (2000) and Whitesides and Grzybowski (2002). There are also recent studies that report important advances on the kinetic control of dynamic self-assembly processes through balancing two opposing forces (Capito et al., 2008; Ladet et al., 2008; Moore and Kraft, 2008).

With the viewpoint of force balance, all three points a, b, and c are the points of self-assembly on the coordination of self-assembly. The concept of force balance makes it possible for us to embrace a wider scope of self-assembly.

1.2. IDENTIFICATION OF BUILDING UNITS

This section provides the foundations for the segmental analysis of self-assembly building units. The concept of the three fundamental segments of self-assembly building units will be presented first, followed by the concept of the two additional segments.

1.2.1. What Is a Self-Assembly Building Unit?

A clear definition of *self-assembly building unit* cannot be easily established because it can cover so many diverse types of entities from atoms to colloidal length scale materials. This may be the reason that there is no general consensus

on a clear-cut definition of self-assembly building unit at this moment. However, based on the diverse and flexible facts of self-assembly building units, it would be safe to say that self-assembly building units are any type of entities that have the capability, by themselves or under the influence of any type of external forces, to be assembled into aggregate states mainly through weak intermolecular or colloidal forces and to keep the states as long as the equilibrium or kinetic condition that makes it possible is not perturbed. There can be cases where strong bonds, including covalent bond, ionic bond, and coordination bond, are involved along with the weak forces. For full information about this fact, please refer to Lee (2008). As mentioned briefly, this can cover a wide range of different types and sizes including atoms, molecules, polymers, and colloidal objects, and even beyond the size of colloidal particles such as macro-size materials. The segmental analyses in the following subsection thus cover all the different types and sizes of self-assembly building units.

1.2.2. Segmental Analysis

1.2.2.1. Three Fundamental Segments. Figure 1-3 shows the schematic representation for three fundamental segments of self-assembly building units. It also shows the possible combinations of those segments that can act as self-assembly building units based on the force balance theory described in the previous section.

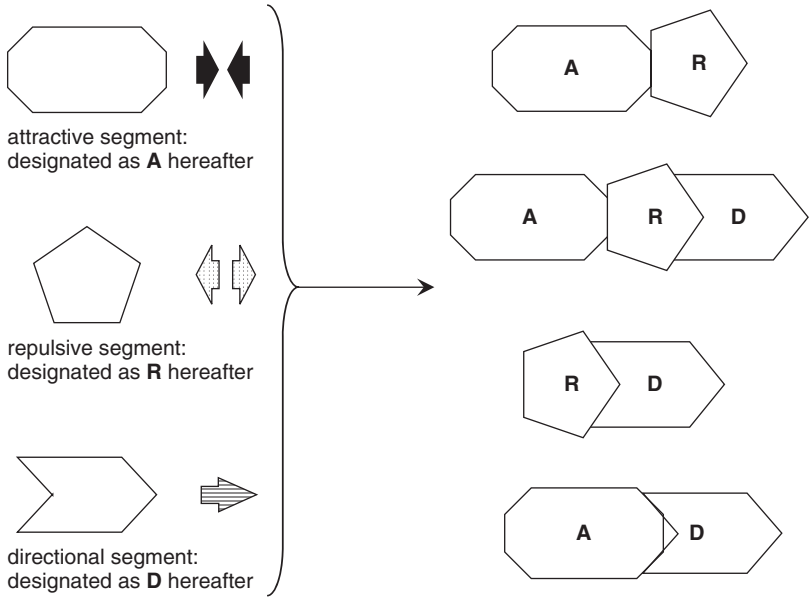

Figure 1-3. Three fundamental segments of self-assembly building units and their possible combinations. Arrows represent the direction of the force between the segments during self-assembly.

Big arrows represent the direction of the force between the segments during self-assembly. These will be used throughout the book. The geometric symbols for each segment are also shown: elongated octagon for attractive segment, pentagon for repulsive segment, and one-sided hexagon-type arrow for directional segment. These will be also used throughout the book. There will be constant adjustments on their sizes and shapes in order to best describe each self-assembly building unit, but the basic characteristic features of these symbols will be the same.

All potential self-assembly building units are composed of three structural segments regardless of their types and sizes: attractive segment, repulsive segment, and directional segment. The attractive segment is the segment (or part) within the building unit that has the capability to attract other attractive segments from other building units. The repulsive segment is the segment within the building unit that has the capability to repel other repulsive segments from other building units. The directional segment is the segment within the building unit that has the capability to direct the self-assembly process toward a certain direction. Direction here means not only a linear type of directional self-assembly but circular or spiral types of self-assembly as well. Figure 1-3 also shows four possible combinations of the three fundamental segments to make self-assembly building units. Force balance theory tells us that, to become a self-assembly process, its building unit should have at least two out of the three fundamental segments so the force balance can be properly set. This means that there can be only four possible combinations. Obviously, two main combinations will be an attractive segment combined with a repulsive segment and an attractive segment combined with a repulsive segment and a directional segment. These two are indeed the most abundant forms of self-assembly building units in reality. Force balance theory also tells us that, with a properly set condition, a repulsive segment combined with a directional segment and an attractive segment combined with a directional segment should also be effective combinations that can make self-assembly building units.

Table 1-1 shows representative examples for attractive, repulsive, and directional segments. It includes the intrinsic components (parts of the building units) that can become each of the three fundamental segments. It also includes the physical, chemical, and conditional factors that can be played as each of the three fundamental segments whenever the condition is properly set. Examples of attractive segments are hydrocarbon and fluorocarbon chains that can induce hydrophobic attractive force in aqueous or aqueous-based solutions. Hydrophobic surface, in this sense, can be an attractive segment since it can also induce hydrophobic attractive force when it is in contact with certain molecules, colloidal particles, or even bulk materials. Charged atoms within self-assembly building units can be an attractive segment whenever the charges that are interacting with it are different. It will be through electrostatic attractive force. Of course, when the charges are the same, they become a repulsive segment that causes an electrostatic repulsion. The same logic holds for the charged surfaces. The structure recognizable groups are molecular or colloidal groups or characteristic structures within self-assembly building units that can induce a host–guest type of interaction. This geometrical interaction certainly attracts the building units and thus makes them an attractive segment.

TABLE 1-1. Intrinsic components that can be each of the three fundamental segments. Physical, chemical, and conditional factors that can act as fundamental segments are also shown. A, R, and D refer to attractive, repulsive, and directional segments, respectively.

	Intrinsic Component	Physical Factor	Chemical Factor	Conditional Factor
A	hydrocarbon chain fluorocarbon chain hydrophobic surface charged atom charged surface structure recognizable group	surface charge solvation physisorption	surface thiolation surface silylation chemisorption surface oxidation surface reduction other surface reactions	concentration evaporation temperature pressure pH
R	bulky group charged atom hydrated atom charged surface	surface charge solvation desorption hydration		concentration temperature pressure pH
D	hydrogen bonding group coordination bonding group structure recognizable group DNA biological group	electric field magnetic field flow physisorption	surface thiolation surface silylation chemisorption surface oxidation surface reduction other surface reactions	evaporation temperature pressure pH

At the same time, most of the attractive interaction occurs in a certain direction that is defined by the overall geometry of those groups. Physical factors for attractive segments include surface charge, solvation, and physisorption. Surface charges that are interacting with should be different ones to become an attractive segment. When they are the same ones, they will become a repulsive segment. The origins of solvation and physisorption processes are different. But the results of the processes certainly can be attractive interactions, which makes them an attractive segment. Some types of solvation process can induce a repulsive interaction. When this is the case, it becomes a repulsive segment. Chemical factors for attractive segment are cases where relatively strong bonds (compared with intermolecular and colloidal forces) induce an attractive interaction. Shown are some representative examples that occur on surfaces. But some types of chemical factor in bulk, for example, thiolation, silylation, or oxidation reaction, can also induce attractive interaction between self-assembly building units, thus becoming an attractive segment. Finally, the conditional factors for an attractive segment include typical experimental conditions that can induce an attractive interaction between self-assembly building units. This includes concentration, evaporation, temperature, pressure, and pH.

As examples of repulsive segments, most of the bulky groups within self-assembly building units can induce the steric effect, which can act as a repulsive interaction. In some cases, the steric effect can act as a directional segment as well. As stated in the previous paragraph, charged atoms and charged surfaces can become a repulsive segment, too. Hydrated atoms are another example of repulsive

segment. They can cause repulsive hydration force. Physical factors for the repulsive segment include the solvation force, which actually has an oscillatory nature, meaning that it can induce both attractive and repulsive interactions and thus can be both an attractive segment and a repulsive segment. Contrary to the adsorption process, a desorption process, which is a process of an adsorbate leaving from the surface of a certain substrate (or adsorbent), can also be understood as a physical factor for repulsive segment. As in cases of attractive segment, most of the conditional factors including concentration, temperature, pressure, and pH can also be used as a repulsive segment.

A directional segment is for directional/functional forces. One typical example that can induce this relatively strong interaction compared with the attractive and repulsive segments (but much weaker than covalent and ionic bonds) is hydrogen bonding. Thus, most of the hydrogen bonding groups belong to a directional segment. With a similar reason, coordination bonding groups are also classified as a directional segment even though their interaction is much stronger than hydrogen bonding. Structure recognizable groups are the pairs of molecular or colloidal groups from two different self-assembly building units that can recognize their geometrical characteristics, which can provide a host–guest type of interaction between them. In most cases, DNA and biological groups within biological systems and biological function-mimic groups within bio-mimetic systems also interact through this host–guest type of interaction. Hence, they all become a directional segment. Many external forces that can have some degree of influence on self-assembly processes have their impacts on self-assembly building units in a linear manner, which makes them a directional physical factor. This includes electric field, magnetic field, and flow. These external force-based factors are usually specific on the physical properties of each self-assembly building unit. For example, magnetic field will have a significant impact only when the self-assembly building unit is susceptible on magnetic field, meaning that the self-assembly building unit (or at least part of it) should be magnetic or paramagnetic. Physisorption is a process that can occur only on a surface of substrates, which means that it will always direct the self-assembly process toward the direction of a given substrate. It thus becomes a directional segment. For the same reason, most of the surface processes that are classified as an attractive segment can be employed as a chemical factor for directional segment. Lastly, conditional factors that can be either an attractive segment or a repulsive segment can also become a conditional factor for directional segment as long as a well-designed experimental condition can ensure the directionality of the assemblies.

This list is certainly not a complete one. As will be stated in the Epilogue at the end of the book, it will take the building up of a huge database to make a complete list for these fundamental segments only.

Figure 1-4 emphasizes the fact that the four possible combinations of the three fundamental segments of self-assembly building units that are shown in Figure 1-3 can cover a wide range of entities as a potential self-assembly building unit. Not only for the testing of existing molecules or colloidal particles as a self-assembly building unit but for the designing of a new molecular or colloidal self-assembly

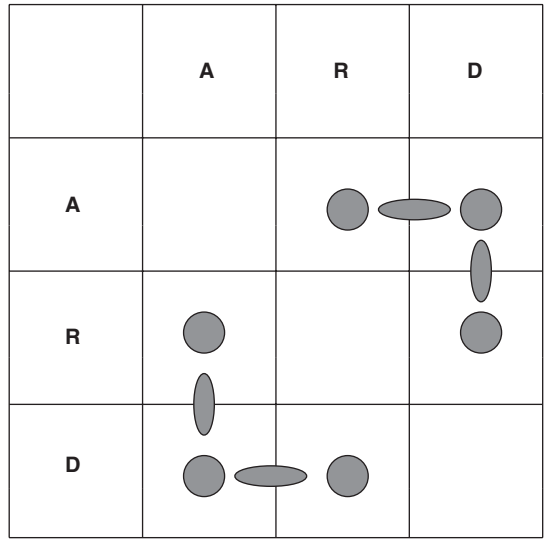

Figure 1-4. The four possible combinations of the three fundamental segments can nicely cover a wide range of entities as a potential self-assembly building unit. **A, R**, and **D** refer to attractive, repulsive, and directional segments, respectively.

building unit for a given condition as well, this fact provides good insight that the "chemical space" that can be explored for potential self-assembly building units is not as narrow as we might have thought. At first hand, as long as the whole or a part of the potential self-assembly building unit fits with one of the four possible combinations of the three fundamental segments, they can be considered to have a reasonable possibility of self-assembly capability. Also, as will be stated throughout the second and third parts of the book, even with the entities that are located in the empty space of the diagram (**A-A**, **R-R**, or **D-D** combination), there is a reasonable possibility that they also can be employed as a potential self-assembly building unit. A key is the selection of proper external force, which will make it possible for us to apply the concept of external force–induced self-assembly.

1.2.2.2. Two Additional Segments. The concept of the three fundamental segments of self-assembly building units was described in the previous subsection. Literally, they are the fundamental segments (parts) that should be present within a potential self-assembly building unit regardless of its types and sizes so that the potential self-assembly building unit becomes an actual self-assembly building unit. The directional segment may not necessarily have to be present all the times. But, as discussed in Table 1-1, they are in many cases easily distinguishable from the attractive segment or the repulsive segment. Also, the directional segment often shares the role of either the attractive segment or the repulsive segment.

To understand and describe the full spectrum of self-assembly, there are also two additional structural features of self-assembly building units that should be taken into account. They are not always present within self-assembly building units. Their

presence among the full spectrum of self-assembly building units is relatively small compared with those that are composed of the four possible combinations of the three fundamental segments. However, once they are present, they have a dramatic impact not only on the whole proceeding of self-assembly processes but on the structures, properties, and functionalities of self-assembled aggregates as well. This provides enough reason to have them classified as another group of self-assembly building unit segments: *two additional segments*.

Figure 1-5 presents the two additional segments of self-assembly building units. They are an asymmetric packing segment and an external force specific functional segment. An asymmetric packing segment is a segment (or a part) within the self-assembly building unit that can induce the packing of the building unit with an asymmetric nature. Without it, most of the self-assembly processes will occur with a symmetric packing between self-assembly building units. Many biological and bio-mimetic self-assembly building units have the asymmetric packing segment. One of the most prominent results from asymmetric packing is the chirality of self-assembled aggregates. As will be discussed in the second part of the book, the self-assembled aggregates that possess a chiral nature, both intrinsic and induced ones, are relatively non-abundant yet give a dramatic morphological diversity, which in turn provides rich possibilities for technological applications. An external force-specific functional segment is a segment (or a part) within the self-assembly building unit that has a functionality whose function (or response)

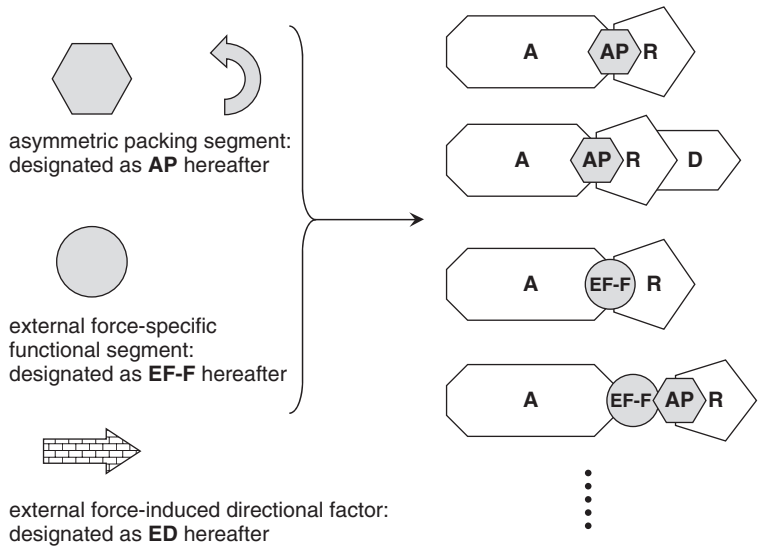

Figure 1-5. Two additional segments of self-assembly building units and their possible combinations with the three fundamental segments. The curved arrow represents the asymmetric packing of self-assembly building units during self-assembly while the blocked-arrow is for external force–induced directional factor. **A, R**, and **D** refer to attractive, repulsive, and directional segments, respectively.

is exclusive on a specific signal (or stimulus) that is provided from outside (often inside, too) the self-assembly system. Symbols of gray-filled hexagon and gray-filled circle are used to represent asymmetric packing and external force–specific functional segments, respectively. These will be used throughout the book.

Figure 1-5 also shows the possible combinations of the two additional segments with the three fundamental segments that can make an effective self-assembly building unit. All four combinations of the three fundamental segments from Figure 1-3 can be combined with either or both of the two additional segments. This makes the total possible combinations for self-assembly building unit, based on this segmental analysis, 16. It implies that, unless a self-assembly building unit cannot fulfill the force balance, all the possible self-assembly building units, whether they exist already or are at the design step, should belong to one of the 16 structural patterns. Therefore, it will be fair to conclude that, unless a potential self-assembly building unit belongs to one of the 16 patterns, it will not work as an effective self-assembly building unit, and thus cannot self-assemble. The only option that can be used is an external force that can overcome the unbalanced force balance between self-assembly building units. Figure 1-5 also shows this external force–induced directional factor. There can be some types of external forces that have their impact on self-assembly building units in a somewhat random manner. But most of the external forces have their impact in a significantly directional manner because their strength and range of interactions with self-assembly building units are comparable to the intermolecular or colloidal interactions between self-assembly building units. This is the logic behind naming it a "directional factor," which is induced only by external force. A blocked-arrow will be used to designate this factor throughout the book. A curved arrow is for an asymmetric packing.

Table 1-2 shows intrinsic components that can be each of the two additional segments. As with the three fundamental segments in Table 1-1, it also presents physical, chemical, and conditional factors that can be employed as additional segments. For an asymmetric packing segment, hydrogen bonding groups and coordination bonding groups are the most abundant examples. They are also listed as a directional segment in Table 1-1. Whenever there is one of these groups within a self-assembly building unit, the self-assembly will occur in a directional manner. But when this directional assembly is distorted for any reason (mostly by an uneven multiple hydrogen or coordination bonding or by the interference of other groups such as the steric group), the self-assembly occurs in an asymmetric manner. The asymmetric manner means that the self-assembly building units are packed in an asymmetric way toward each other. Structure recognizable group is also listed as a directional segment in Table 1-1. For the same reason, this group can also induce an asymmetric packing between self-assembly building units whenever there are factors that cause unevenness in its directional nature. It thus becomes an asymmetric packing segment. Asymmetric structure might be the most characteristic component for an asymmetric packing segment. In almost all cases, the self-assembly building units that have at least one of the asymmetric structures are packed in an asymmetric manner during their self-assembly processes. Chiral center is the most distinguishable example for this type of asymmetric packing segment. When

TABLE 1-2. Intrinsic components that can be each of the additional segments. Physical, chemical, and conditional factors that can act as additional segments are also shown. AP, EF-F, and ED refer to asymmetric packing segment, external force–specific functional segment, and external force–induced directional factor, respectively.

	Intrinsic Component	Physical Factor	Chemical Factor	Conditional Factor
AP	hydrogen bonding group coordination bonding group asymmetric structure structure recognizable group	physisorption	chemisorption	
EF-F	azo group disulfide group ferrocenyl group *cis–trans* group charged surface magnetic field-sensitive component electric field-sensitive component			
ED		electric field magnetic field flow epitaxial matching		concentration evaporation temperature pressure pH ionic strength ultrasound UV, visible, laser

some types of adsorbates are adsorbed on certain types of surfaces, mostly solid surfaces, there can be a break in the symmetry of the adsorbates. This symmetry breaking is dependent on each system and experimental condition. But it can happen via both physisorption and chemisorption, and once it happens, the adsorbates (self-assembly building units) are packed on the surfaces in an asymmetric manner. Thus, both physisorption and chemisorption can become an asymmetric packing segment. The former is a physical factor for asymmetric packing segment while the latter is a chemical factor. Few conditional factors are known to be a prominent asymmetric packing segment except for the rare case where the fluctuation of local concentration can cause some degree of asymmetric packing.

The external force–specific functional segment is a segment within self-assembly building unit that responds to an external signal, which provides the self-assembly building unit an external force–induced interaction. One of the typical examples is the azo group–based segment, which can respond to light through *cis-trans* isomerization. The disulfide group is sensitive on catalytic reaction. The ferrocenyl group is sensitive on electrochemical signal. The *cis-trans* group always has a potential for an external force specific functional segment as long as it can show a clear *cis-trans* transformation in responding to a specific external signal. Charged surfaces were typical examples for an attractive segment and a repulsive segment

in Table 1-1. In many cases, they can also be sensitive on the changes in solution conditions such as pH or ionic strength. They thus can become an external force–specific functional segment as well. Whenever there is a magnetic field-sensitive or an electric field-sensitive component (or part) within a self-assembly building unit, it can be subject to any changes in a magnetic field or an electric field. This will give the building unit a newly induced interaction in addition to the intrinsic ones, which makes the component an external force–specific functional segment.

The external fields that induce the changes in the interactions between self-assembly building units are the physical factor for directional segment (Table 1-1). At the same time, they are the physical factor for the external force–induced directional factor as well. This is the same as with the others, including flow and epitaxial matching. When the primary emphasis is their impact on the directional interaction between self-assembly building units, they should be interpreted as a directional segment. But when their impact on the directionality of an entire self-assembly process is the primary concern, they should be viewed as an external force–induced directional factor, which in turn can give us a specific understanding of the changes in the properties and structures of self-assembled aggregates. The same logic is applied for the conditional factors for the external force–induced directional factor. Most of them can become an attractive segment, a repulsive segment, or a directional segment, depending on how we see the self-assembly process and self-assembled aggregate. Practical examples of this classification will be shown throughout the second and third parts of the book.

1.3. IMPLICATION OF BUILDING UNIT STRUCTURES FOR SELF-ASSEMBLIES

The segmental analysis from the previous section can be used to set up a general rule between the five segments. It is relatively easy to draw and the outcome is simple and systematic. It will allow us to grasp commonalities between the different self-assembly systems that may be seemingly unrelated and complicated.

Figure 1-6 shows the general rules between the five segments. Let us assume that the center point (gray circle) is the point of the initial force balance between certain self-assembly building units. First, the horizontal arrow shows the self-assembly tendency when either an attractive segment or a repulsive segment (or both of them) is varied. Whenever an attractive segment is increased (meaning a more attractive segment within a self-assembly building unit or more favorable factor or condition for an attractive interaction) from the point of initial force balance while a repulsive segment remains the same, the self-assembly becomes more favorable. Whenever an attractive segment is increased while a repulsive segment is decreased, the self-assembly becomes even more favorable. In both cases, self-assembly building units simply have more attractive force to work with. Less favorable self-assembly occurs when the segmental situation is exactly opposite. Whenever an attractive segment is decreased while a repulsive segment remains the

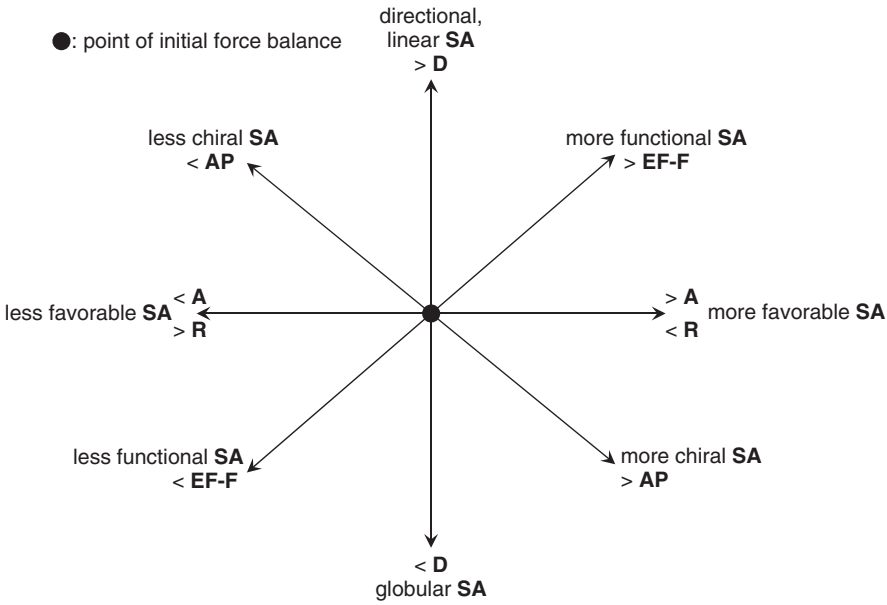

Figure 1-6. General rules regarding the fundamental and additional segments of self-assembly building units that cover most of the self-assembly processes. **SA** is short for *self-assembly*. **A, R, D, AP**, and **EF-F** refer to attractive, repulsive, directional, asymmetric packing, and external force–specific functional segments, respectively.

same, the self-assembly becomes less favorable. Whenever an attractive segment is decreased while a repulsive segment is increased, the self-assembly becomes even less favorable. There is simply less attractive force that can attract the self-assembly building units together. When both an attractive segment and a repulsive segment are varied on this arrow, the favorability is determined simply by which segment overcomes which. If an attractive segment overcomes a repulsive segment, it will be more favorable. The opposite situation will make the self-assembly less favorable. This rule almost always makes the case right, which means that it works well regardless of the types and sizes of self-assembly building units. More favorable self-assembly is usually reflected by smaller critical micellar concentration (*cmc*) (for amphiphiles), smaller critical aggregation number (*can*) (for colloidal particles), bigger aggregation number, and bigger size of self-assembled aggregates. (A full definition of *cmc* and *can*, and the clarification between these two terms will be presented in Subsections 3.3.1 and 3.3.2.) Less favorable self-assembly produces greater *cmc* and *can*, smaller aggregation number, and smaller size of self-assembled aggregates.

The vertical arrow is for the self-assembly systems with a directional segment. Whenever there is a more directional segment (starting from the point of initial force balance), the self-assembly has a high possibility becoming a directional and linear one. Meanwhile, whenever a directional segment is decreased from the point

of initial force balance, the self-assembly becomes less directional or a globular one. This is always the case along the attractive segment–repulsive segment (**A-R**) horizontal line as long as the attractive segment–repulsive segment balance is not disturbed by the directional segment to the degree of disrupting the whole attractive segment–repulsive segment–directional segment (**A-R-D**) balance.

The same general rules can be made for an external force–specific functional segment and an asymmetric packing segment. When a more external force–specific functional segment is employed on a self-assembly building unit (starting from the point of initial force balance), the self-assembly simply will be more functional. A less external force–specific functional segment induces less functional self-assembly. A more asymmetric packing segment results in a more chiral self-assembly while a less asymmetric packing segment should induce a less chiral self-assembly. For both an external force–specific functional segment and an asymmetric packing segment, this relation is always the case on the entire two-dimensional area of the attractive segment–repulsive segment–directional segment (**A-R-D**) balance as long as this three-way balance is not disturbed by the external force–specific functional segment or the asymmetric packing segment (or by both) to the degree of disrupting the whole force balance.

1.4. GENERAL ASSEMBLY DIAGRAM

Now with the knowledge of the general rules among the three fundamental segments and the two additional segments from the previous section, the general tendency of a variety of different self-assemblies can be envisioned. There can be some discrepancies depending on the specific nature of self-assembly systems, which might not allow us to follow the specificity of the self-assembly processes. However, as will be seen throughout the second part of the book, this general tendency provides a reasonable explanation and prediction not only for the changes in the self-assembly processes but for the formation of the self-assembled aggregates as well. It is useful in a wide range of different types and sizes of self-assembly building units and gives a reasonable applicability when it is applied for nanotechnology systems.

First, Table 1-3 shows different types of self-assemblies and their typical examples. More details can be found in (Lee, 2008). This classification of self-assembly is primarily based on the size of the building units (atomic, molecular, polymeric, and colloidal), the origin of the building units (biological and bio-mimetic), the substrate where the self-assembly takes place (surface/interface), and how the force balance is achieved (external force-induced). Along with typical examples of self-assembled systems for each type of self-assembly, some examples of thermodynamic and kinetic self-assembled systems are also included.

Figure 1-7 shows the general tendency of the different types of self-assemblies. It shows how the general rules between the fundamental and additional segments shown in Figure 1-6 can be applied for the different types of self-assemblies shown in Table 1-3. First, most of the molecular and colloidal self-assemblies

TABLE 1-3. Different types of self-assemblies and some typical examples of their self-assembled systems.

Self-Assembly	Self-Assembled System
atomic	quantum dot, nanoisland
molecular	micelle, vesicle, emulsion
polymeric	polyelectrolyte layered film
colloidal	colloidal crystal, sol
biological	cell membrane, protein
bio-mimetic	chiral gel, organic nanotube
surface/interface	self-assembled monolayer, film
external force induced	electrophoretic gel
thermodynamic	micelle, microemulsion
kinetic	macroemulsion, sol, gel

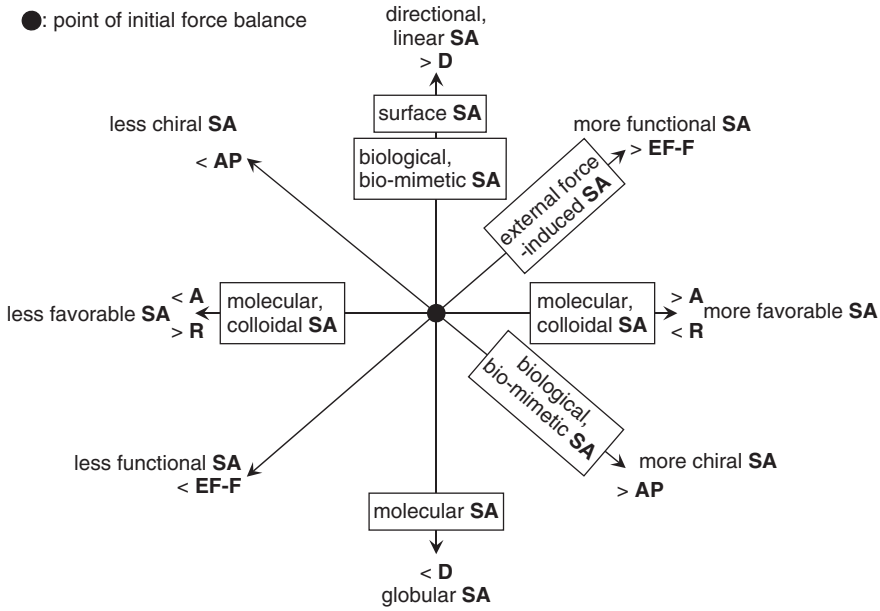

Figure 1-7. General tendency of the different types of self-assemblies. **SA** is short for self-assembly. **A, R, D, AP**, and **EF-F** refer to attractive, repulsive, directional, asymmetric packing, and external force–specific functional segments, respectively.

are well explained by following the general rules between the segments along the horizontal arrow. Once the point of initial force balance is identified, which means that the self-assembly of a "reference" building unit is determined, the effect of changes in an attractive segment and a repulsive segment can be well predicted. The changes and reasonable estimation of the self-assembly parameters can be made by identifying the changes in each segment of the self-assembly building unit and following the general rules between them. The parameters here

include *cmc*, *can*, aggregation number, counterion binding, the sizes and shapes of self-assembled aggregates, and so forth.

Most of the biological and bio-mimetic self-assemblies take place in a directional manner because most of their self-assembly building units have at least one directional segment. Surface self-assembly, in many cases of self-assembly building units, whether they have a directional segment or not, also occurs in a directional manner. The interaction between the surface and the building units is comparable to the interaction between the building units, which directs them to be assembled along the direction of the surface. These directional self-assemblies can also be reasonably followed by identifying the directional segment and following the general rules in Figure 1-6. Three segments should be considered: an attractive segment, a repulsive segment, and a directional segment. As a more directional segment is identified within a self-assembly building unit, the self-assembly will occur in a more directional manner. Subsequent changes can also be followed as the assembly progresses. This rule is valid for the entire area that starts from the horizontal arrow. It means that no matter where the self-assembly building unit of interest is located on the line of the attractive segment–repulsive segment (**A-R**) balance (horizontal arrow), the main work that is needed to predict the self-assembly is identifying the directional segment and following its impact along the vertical arrow. It is rare, but there can be a case of a less directional segment. This usually happens when molecular self-assemblies face a significant disruption of force balance by any means. It can also happen if there is any external force imposed on surfaces or on biological/bio-mimetic self-assemblies and this external force is strong enough to overcome the impact of the directional segment within self-assembly building units. The self-assemblies then should be followed along the vertical arrow downward.

Another characteristic feature of the biological and bio-mimetic self-assemblies, in addition to their directionality, is their hierarchy, which comes from the fact that most of their building units have an asymmetric packing segment. Many of them have two or more asymmetric packing segments. A more asymmetric packing segment can be interpreted as a more chiral self-assembly by following the diagonal arrow. If an asymmetric packing segment is reduced from a certain self-assembly building unit having multiple asymmetric packing segments, its less chiral self-assembly can be followed by the upward diagonal arrow of an asymmetric packing segment. It all starts either by identifying the point of initial force balance and adding the segments that are needed or by identifying a known self-assembly system as a reference system. By simply counting whether a new self-assembly system of interest has more (or less) asymmetric packing segments, the self-assembly process and subsequent results can be reasonably estimated.

Functional self-assembly is mainly related to the presence of an external force–specific functional segment within self-assembly building units. Many of the biological and bio-mimetic self-assemblies can be functional, too. They are subject to the external force that is sensitive on a particular external force–specific functional segment. The same rules are applied for this. Once it is identified that there is an external force–specific functional segment within self-assembly building unit, the

self-assembly is, in most cases, almost linearly responding to the parameters of the external force that is specific on that external force–specific functional segment. The difference from the other cases that include the attractive segment–repulsive segment (**A-R**), attractive segment–repulsive segment–directional segment (**A-R-D**), or asymmetric packing segment (**AP**) arrow is that, depending on the specific nature of the external force and self-assembly building unit, this functional self-assembly can have a certain window of operation. More details on this issue will be given in Chapters 8 and 9.

Figure 1-8 presents a conceptual universal diagram for self-assembly. A practical following of self-assembly processes can be made with this diagram. The first step is finding the point of initial force balance. This can be achieved with a reference self-assembly system. (It may be said that this is the same idea of using internal references to determine the correct chemical shifts in nuclear magnetic resonance [NMR] spectra.) Let us assume that we have a well-known self-assembly system whose self-assembly building unit is composed of one attractive segment and one repulsive segment. Then, it should be possible to obtain all the self-assembly parameters including *cmc* (or *can*) and aggregation number. Now let us place this self-assembly building unit and its force balance between the attractive and repulsive segments at the point of initial force balance (point 1). This is our reference self-assembly system. Let us then assume that we have a new compound (or colloidal particle) that looks like a potentially good candidate for self-assembly. Analyze its fundamental and additional segments. If the result directs the segmental

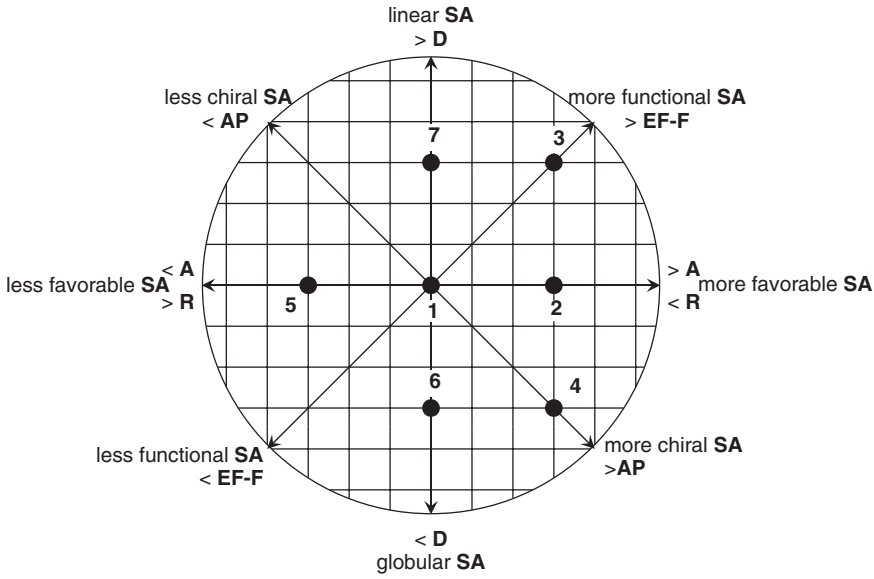

Figure 1-8. Conceptual universal diagram for self-assembly. **SA** is short for self-assembly. **A, R, D, AP**, and **EF-F** refer to attractive, repulsive, directional, asymmetric packing, and external force–specific functional segments, respectively.

structure to the point of more favorable self-assembly (point 2), this compound (or colloidal particle) will self-assemble. The *cmc* (or *can*) will be lower than the one of reference, the aggregation number will be higher than the one of reference, and the size of the self-assembled aggregate will be bigger than the one of reference. If the result, on the other hand, directs it to the point of less favorable self-assembly (point 5), this compound (or colloidal particle) will still self-assemble but with higher *cmc* (or *can*) than the one of reference, smaller aggregation number than the one of reference, and smaller size of the self-assembled aggregate than the one of reference. If the new compound (or colloidal particle) turns out to have too high a ratio of attractive segment over repulsive segment, it will precipitate out rather than self-assemble. Similarly, if it turns out to have too high a ratio of repulsive segment over attractive segment, it will not self-assemble at all. It will make a homogeneous solution or a stable colloidal sol.

If the new compound is analyzed to have a directional segment with the same attractive and repulsive segments as those of the reference system, it will self-assemble with a clear directionality (point 7). Its *cmc* (or *can*) will be usually lower than the one of reference, the aggregation number will be usually higher than the one of reference, and the size of the self-assembled aggregate will be usually bigger than the one of reference. There will be a very high possibility that the shape of the self-assembled aggregate will be much more linear (distorted or linearly grown from a spherical [or nearly spherical] one at point 1). Point 6 is for the opposite situation. When the new compound is analyzed to have a less directional segment than the one of reference, it actually means that it does not have any directional segment. However, when a physical, chemical, or conditional factor directs (on the diagram) that its attractive segment–repulsive segment (**A-R**) balance is disrupted directionally (or in an uneven manner) as if it has a less directional segment, it will still self-assemble, but its *cmc* (or *can*) will be higher than the one of reference, its aggregation number will be smaller than the one of reference, and the size of the self-assembled aggregate will be smaller than the one of reference. There also will be a high possibility that the self-assembled aggregate will have a globular shape.

Now, let us go back to point 2 on the attractive segment–repulsive segment (**A-R**) balance arrow. And let us assume that the segmental analysis shows that the new compound (or colloidal particle) has an external force–specific functional segment with the same attractive and repulsive segments as those of point 2. Point 3 on the diagram shows this situation. Interpretation by following force balance tells us that it will self-assemble and the self-assembly now becomes functional. The favorability of the self-assembly can be determined by simple consideration of the impact of the external force–specific functional segment on the other two segments (attractive and repulsive segments). The variation in the self-assembly parameters can also be determined by following that. The external force that is specific on that external force–specific functional segment will make the functionality more practical. This includes the fine tuning of *cmc* (or *can*), the control of aggregation

number, the control of the size and shape of the self-assembled aggregate, and even the control of assemble–disassemble processes.

Finally, let us go back to point 2 again and assume that the segmental analysis shows that the new compound (or colloidal particle) has an asymmetric packing segment with the same attractive and repulsive segments as those of point 2. Point 4 represents this situation. The new compound has an attractive segment and a repulsive segment and is located on the right-hand side from the point of initial force balance (point 1). This means that it is on the side of more favorable self-assembly. Based on the concept of force balance, this suggests that this new compound will self-assemble under the same experimental conditions as the one for the point 2. However, since it now has an asymmetric packing segment, the self-assembly will become chiral. In other words, the self-assembly has a higher change of chiral self-assembly processes and the self-assembled aggregate has a very high possibility of having chiral structures. As with cases having an external force–specific functional segment, the favorability of the self-assembly will be determined by the impact of the asymmetric packing segment on the overall shift in force balance. Usually, an asymmetric packing segment acts favorably for the overall force balance. Most of the asymmetric packing segment generating groups enforce an attractive segment or even become a new attractive segment when there is no attractive segment within the self-assembly building unit. In many cases, the asymmetric packing segment generating groups also enforce a directional segment or even become a new directional segment. However, the asymmetric packing segment generating groups rarely enforce a repulsive segment or become a new repulsive segment except for cases where their structures are too bulky, so that the steric effect can play a significant role in the overall force balance. Thus, the self-assembly on point 4 usually generates smaller *cmc* (or *can*) than the one of reference, a higher aggregation number than the one of reference, and more diverse and bigger morphologies of the self-assembled aggregate than the one of reference.

This universal diagram for self-assembly is conceptual. The exact form of the diagram that works for all of the self-assembly systems has not yet been established. However, this conceptual diagram covers many different self-assembly systems with a wide range of sizes and types of self-assembly building units. Once the reference point (point of initial force balance) is determined, it provides the general tendency of self-assembly processes and self-assembled aggregates in a controlled manner with reasonable accuracy. Furthermore, it works almost like a typical phase diagram, which makes it easy to use. Outside the boundary, there will be no self-assembly. Inside the boundary, there always will be self-assembly. We can simply follow the exact line of the grid from the reference point to the point of interest or just jump to the point of interest. The self-assembly systems at the points in between these two points (of reference and of interest) will almost always have a self-assembly tendency in between those at the two points and the structures and properties of the self-assembled aggregates in between those at the two points as well. Plenty of detailed examples will be presented throughout the second and third parts of the book.

1.5. COLLECTION OF BUILDING UNITS

This section provides a collection of self-assembly building units. They are collected from a wide range of different journals and books published up until 2010. They are well studied for their self-assembly capabilities and their basic self-assembly parameters (*cmc, can*, aggregation number) are well documented. For most of them, the self-assembly can take place both in solution and at the surface as long as the experimental conditions are properly set. For some of them, the self-assembly parameters are not well reported mostly because of their physical characteristics in specific conditions such as the solubility issue and because of their complexity of assembly. But their self-assembly itself is well established.

The self-assembly building units in this section are divided into four different groups and presented in 10 separate tables. This classification is based on the segmental analysis of the self-assembly building units that was presented in the previous four sections of this chapter. The first group is basic self-assembly building units. These are the building units whose structures have only two fundamental segments for self-assembly: attractive and repulsive segments. The second group is those having a directional segment so that they self-assemble in a directional manner. The third group has an asymmetric packing segment. And the last group is for the building units that have an external force–specific functional segment so that their self-assembly is influenced by external stimuli. As will be discussed in the second part of the book, the pattern of self-assembly of the building units within the same group is very similar and the outcomes of their self-assembly, such as the morphologies and sizes of the self-assembled aggregates, can be understood with a similar set of schemes. This unified general picture of self-assembly based on the structure of its building units can provide a logical way of identifying the commonalities and differences between different self-assembly systems. This in turn provides a practical way of applying the self-assembly processes and aggregates for a variety of nanotechnology systems. This will be discussed in the third part of the book.

1.5.1. Basic Building Units

Tables 1-4, and 1-5 provide the collection of self-assembly building units that have the combination of attractive and repulsive segments. For those in Table 1-4, the repulsive segment is an intrinsic one, which means it is a part of their structures. This may be the most abundant and well-studied type of self-assembly building units. Many surfactants, ionic liquids, polyelectrolytes, and colloidal or nanoparticles with natural or modified surface charges belong to this one. Chapter 3 covers the fundamental principles of their self-assembly both in solution and at the surface. Chapter 4 covers their multi-step self-assembly. And Chapter 5 has the structural issues of their self-assembled aggregates. For those in Table 1-5, the repulsive segment is conditional. This repulsive segment is not a part of their structures. The attractive segment is their only intrinsic segment. However, whenever the simple experimental conditions such as pH and ionic strength are properly met for their

TABLE 1-4. Collection of the self-assembly building units that have the combination of attractive (A) and repulsive (R) segments. m and c indicate molecular and colloidal building units, respectively. surf., i.l., and poly. are short for surfactant, ionic liquid, and polyelectrolyte, respectively. n is an alkyl chain length, and the most common ones are shown for each homologue series.

Name	Kind	Group
alkyltrimethylammonium bromide (n = decyl - octadecyl)	m	surf.
alkyltrimethylammonium chloride (n = decyl - octadecyl)	m	surf.
alkyltrimethylammonium tosylate (n = decyl - octadecyl)	m	surf.
alkylpyridinium bromide (n = decyl - octadecyl)	m	surf.
alkylpyridinium chloride (n = decyl - octadecyl)	m	surf.
alkane(n_1)diyl-α,ω-bis(alkyl(n_2)dimethylammonium bromide) (n_1 = ethyl - octyl; n_2 = decyl - octadecyl)	m	surf.
lithium alkyl sulfate (n = octyl - hexadecyl)	m	surf.
sodium alkyl sulfate (n = octyl - hexadecyl)	m	surf.
cesium alkyl sulfate (n = octyl - hexadecyl)	m	surf.
sodium alkyl sulfonate (n = octyl - hexadecyl)	m	surf.
sodium alkyl benzenesulfonate (n = octyl - hexadecyl)	m	surf.
sodium dialkyl benzenesulfonate (n = octyl - hexadecyl)	m	surf.
alkyl oligo(oxyethylene) ether (n = octyl - octadecyl)	m	surf.
α-dodecyl-ω-hydroxypoly(oxyethylene) (Brij-, Laureth series)	m	surf.
poly(oxyethylene glycol)-*p*-tert-octylphenyl ether (Triton X series)	m	surf.
nonylphenol ethoxylate (Igepal, NP, Tergitol, Triton N series)	m	surf.
dimethyldialkylammonium bromide (n = octyl - octadecyl)	m	surf.
bis(2-ethylhexyl) sulfosuccinate sodium salt (aerosol OT)	m	surf.
bis(2-ethylhexyl) sulfosuccinic acid iron (III) salt	m	surf.
bis(2-ethylhexyl) sulfosuccinic acid iron (II) salt	m	surf.
1-alkyl-3-methylimidazolium salt (n = butyl - octadecyl)[a]	m	i.l.
1-alkyl-3-methylpyridinium salt (n = butyl - octadecyl)[a]	m	i.l.
1-alkyl-4-methylpyridinium salt (n = butyl - octadecyl)[a]	m	i.l.
1-alkyl-1-methylpyrrolidinium salt (n = butyl - octadecyl)[a]	m	i.l.
1-alkyl-1-methylpiperidinium salt (n = butyl - octadecyl)[a]	m	i.l.
linear poly(ethyleneimine)	p	poly.
poly(4-vinylpyridine propylsulfobetaine)	p	poly.
poly(allylamine hydrochloride)	p	poly.
poly(sodium 4-styrenesulfonate)	p	poly.
poly(L-lysine)	p	poly.
poly(vinylpyrrolidone)	p	poly.
poly(styrene-*block*-4-vinylpyridine)	p	
pluronic (ethylene oxide-propylene oxide triblock copolymers)	p	
per(or semi)fluorinated alkyl oligo(oxyethylene) ether (n = hexyl - octadecyl) e.g., Zonyl FSN-100 (ethoxylated perfluorohexylethanol)	m	surf.
semifluorinated n-alkanes (commonly denoted as FnHm) e.g., perfluorooctyl n-octadecane	m	
silica nanoparticle (with natural surface silanol group)	c	
silica nanoparticle (with surface charge or surface hydroxylated)	c	
metal nanoparticles:[b] e.g., gold, silver, platinum, rhodium, copper, cadmium, aluminum, lead, iron, osmium, iridium, titanium, ruthenium, molybdenum	c	
semiconductor nanoparticles:[b] e.g., silicon, germanium, gallium, antimony, tin	c	
metal oxide nanoparticles:[b]	c	

TABLE 1-4. (*Continued*)

Name	Kind	Group
e.g., silica, zirconia, ceria, hafnia, alumina, titania, tungsten oxide, iron oxide, maghemite, zinc oxide, cobalt oxide, samarium oxide, manganese oxide, nickel oxide, gallium oxide, molybdenum oxide		
metal hydroxide nanoparticles:[b]	c	
e.g., aluminum hydroxide (gibbsite[c]), nickel hydroxide		
metal hydroxide oxide nanoparticles:[b]	c	
e.g., aluminum hydroxide oxide, manganese hydroxide oxide, nickel hydroxide oxide, iron hydroxide oxide, goethite, yttrium hydroxide oxide		
metal chloride nanoparticles:[b]	c	
e.g., silver chloride		
(metal) nitride nanoparticles:[b]	c	
e.g., boron nitride, carbon nitride, aluminum nitride, silicon nitride		
(metal) carbide (nitride) nanoparticles:[b]	c	
e.g., silicon carbide, boron carbide nitride		
metal sulfide nanoparticles:[b]	c	
e.g., tungsten sulfide, molybdenum sulfide, lead sulfide, zinc sulfide		
metal phosphates:[b]	c	
e.g., zirconium phosphate		
metal phosphides:[b]	c	
e.g., indium phosphide		
metal borides:[b]	c	
e.g., titanium boride, zirconium boride, tungsten boride		
bimetallic nanoparticles:[b]	c	
e.g., gallium arsenide, cadmium telluride, bismuth telluride, cadmium selenide		
alloy nanoparticles:[b]	c	
e.g., gold-platinum, palladium-platinum, nickel-platinum		
multi-metal oxide nanoparticles:[b]	c	
e.g., barium titanium oxide, cobalt iron oxide		
polymeric nanoparticles:[b]	c	
e.g., polystyrene, poly(methyl methacrylate)		
Keggin polyoxometalate clusters:	c	
e.g., tungstomanganatesilicate ($MnSiW_{11}O_{40}^{8-}$), etc.		

[a]Common anions for these amphiphilic ionic liquids include chloride, bromide, nitrate, iodide, triflate, perchlorate, perfluoroacetate, acetate, tetrafluoroborate, hexafluorophosphate, and methylsulfate;
[b]with surface charges;
[c]mineral.

TABLE 1-5. Collection of the self-assembly building units that have the combination of attractive (A) and conditional repulsive (R^c) segments. m and c indicate molecular and colloidal building units, respectively.

Name	Kind
All nanoparticles in Table 1-4 without (or with minimal) surface charges or groups,	
carbon nanotube (single-, double-, multi-walled)	c
graphene	c
buckminsterfullerene (C_{60})	m
fullerene (C_{70})	m

self-assembly, they can induce a repulsive segment of their own. Many colloidal self-assembly building units have this type of segmental structure, and play an important role in the design and application of nanotechnology systems. More details are presented in Figures 8-3(b), 11.2(b, c), 12.2(c, d), 13.2(b), and 14.4(c).

1.5.2. Directionally Assembling Building Units

Tables 1-6, 1-7, 1-8, and 1-9 provide the collection of self-assembly building units whose segment combinations have at least one directional segment. For those in Tables 1-6, 1-7, and 1-8, this directional segment is intrinsic; thus it is a part of their structure. Some special surfactants, liquid crystals, and dye molecules have

TABLE 1-6. Collection of the self-assembly building units that have the combination of attractive (A), repulsive (R), and directional (D) segments. m and p indicate molecular and polymeric building units, respectively; surf. and l.c. are short for surfactant and liquid crystal, respectively.

Name	Kind	Group
dodecyl(2-hydroxyethyl)dimethylammonium bromide	m	surf.
4-cyano-4′-n-pentyl-l,1′-biphenyl (5CB)	m	l.c.
4-cyano-4′-n-octyl-l,1′-biphenyl (8CB)	m	l.c.
diindenoperylene	m	dye
3,4,9,10-perylenetetracarboxylic acid	m	dye
3,4,9,10-perylenetetracarboxylic diimide (PTCDI)	m	dye
1,4-bis(2,4-diamino-1,3,5-triazine)benzene[a]	m	
coumarin 460	m	dye
fluorescein	m	dye
rhodamine B	m	dye
porphines (porphyrins)	m	dye
phthalocyanines	m	dye
e.g., copper phthalocyanine, zinc phthalocyanine		
polyethylene oxide-chains, with thiol end group (PEO chain, thiolated)[b]	p	
e.g., poly(ethylene glycol) 11-mercaptoundecyl methyl ether		
dendrons	p	

[a]This is a unique partner building unit that forms a multi–hydrogen bond–induced molecular nanowire with PTCDI.
[b]Directional segment is conditional.

TABLE 1-7. Collection of the self-assembly building units that have the combination of repulsive (R) and directional (D) segments. m indicates molecular building unit.

Name	Kind
carboxymethyl trimethylammonium bromide	m
2-carboxyethyl trimethylammonium bromide	m
3-carboxypropyl trimethylammonium bromide	m
4-carboxybutyl trimethylammonium bromide	m
carboxymethyl trimethylammonium chloride	m
2-carboxyethyl trimethylammonium chloride	m
3-carboxypropyl trimethylammonium chloride	m
4-carboxybutyl trimethylammonium chloride	m

TABLE 1-8. Collection of the self-assembly building units that have the combination of attractive (A) and directional (D) segments. m, b, and b-m indicate molecular, biological, and bio-mimetic building units, respectively; n is an alkyl chain length, and the most common ones are shown for each homologue series; surf. is short for surfactant.

Name	Kind	Group
n-alkanoic acid (n = octyl - octadecyl) e.g., caprylic acid (octanoic acid) capric acid (decanoic acid) lauric acid (dodecanoic acid) myristic acid (tetradecanoic acid) palmitic acid (hexadecanoic acid) stearic acid (octadecanoic acid)	m	
n-perfluoroalkanoic acid (n = octyl - octadecyl)	m	
n-alkylphosphonic acid (n = octyl - octadecyl)	m	
retinoic acid (all-trans-Vitamin A acid)	b	
n-alkanol (n = octyl - octadecyl)	m	
glycerol monolaurate	b-m	surf.
glycerol monostearate	b-m	surf.
ω-mercapto alkanol (n = hexyl - octadecyl)[a]	m	
ω-mercapto alkanoic acid (n = hexyl - octadecyl)[a]	m	
alkanol, ω-(triethoxysilyl)- (n = hexyl - octadecyl)l)[a]	m	
alkanol, ω-(trimethoxysilyl)- (n = hexyl - octadecyl)[a]	m	
alkanol, ω-(trichlorosilyl)- (n = hexyl - octadecyl)[a]	m	
alkanoic acid, ω-(triethoxysilyl)- (n = hexyl - octadecyl)[a]	m	
alkanoic acid, ω-(trimethoxysilyl)- (n = hexyl - octadecyl)[a]	m	
alkanoic acid, ω-(trichlorosilyl)- (n = hexyl - octadecyl)[a]	m	

[a]These building units have conditional directional segment (**D**^{c}) as well. (See Table 1-9.)

TABLE 1-9. Collection of the self-assembly building units that have the combination of attractive (A) and conditional directional (D^{c}) segments. m indicates molecular building unit; n is an alkyl chain length, and the most common ones are shown for each homologue series.

Name	Kind
n-alkanethiol (n = hexyl - octadecyl)	m
α,ω-alkanedithiol (n = hexyl - octadecyl)	m
ω-mercapto alkanol (n = hexyl - octadecyl)[a]	m
ω-mercapto alkanoic acid (n = hexyl - octadecyl)[a]	m
ω-mercaptoalkanetrimethoxysilane (n = hexyl - octadecyl)	m
alkanol, ω-(triethoxysilyl)- (n = hexyl - octadecyl)[a]	m
alkanol, ω-(trimethoxysilyl)- (n = hexyl - octadecyl)[a]	m
alkanol, ω-(trichlorosilyl)- (n = hexyl - octadecyl)[a]	m
alkanoic acid, ω-(triethoxysilyl)- (n = hexyl - octadecyl)[a]	m
alkanoic acid, ω-(trimethoxysilyl)- (n = hexyl - octadecyl)[a]	m
alkanoic acid, ω-(trichlorosilyl)- (n = hexyl - octadecyl)[a]	m
n-alkyltriethoxysilane (n = hexyl - eicosyl)	m
n-alkyltrimethoxysilane (n = hexyl - eicosyl)	m
n-alkyltrichlorosilane (n = hexyl - eicosyl)	m
n-alkyldiethoxychlorosilane (n = hexyl - eicosyl)	m
n-alkyldimethoxychlorosilane (n = hexyl - eicosyl)	m
(perfluoro-1,1,2,2-tetrahydroalkyl)trichlorosilane (n = octyl - octadecyl)	m
n-alkylmercury acetate (n = octyl - hexadecyl)	m
n-alkylmercury chloride (n = octyl - hexadecyl)	m
tetrathiafulvalene	m

[a]These building units have intrinsic directional segment (**D**) as well. (See Table 1-8.)

this type of structure. Chapter 5 has in-depth discussions on the characteristics of self-assembly processes and self-assembled aggregates that can be expected from the self-assembly building units with directional segments. For those in Table 1-9, the directional segment is conditional. Unlike for the conditional repulsive segment in the previous subsection, the conditional directional segments of this type of self-assembly building units are a part of their structures. But their directional assembly capability is expressed only when they meet with a specific type of substrates. Self-assembly having this nature provides some specific advantages for many nanotechnology systems. Figures 12-2(a), 13.2(a), and 14.4(a, f) provide more details about this.

1.5.3. Asymmetrically Packing Building Units

When the self-assembly building units have an asymmetric packing segment within their structures, their self-assembly processes become more chiral and the structures of their self-assembled aggregates become much more diversified. Tables 1-10, 1-11, and 1-12 provide the collection of self-assembly building units that have at least one asymmetric packing segment. Their numbers are relatively small compared with the basic self-assembly building units. And most of them originate from biological systems or have bio-mimetic natures. Lipids, proteins, and peptides are typical groups of building units of this type. There are a few surfactants that have this type of segmental structure as well. Chapter 6 covers the impact of this asymmetric packing segment on the self-assembly aggregates formed in solution and at the surface. Its role in the design and application of nanotechnology systems is presented throughout the third part of the book. Figures 11-2(a), 12.2(b) and 14.4 (i, j) have more detailed structural analyses for this type of building unit.

1.5.4. Functional Building Units

Table 1-13 presents the collection of self-assembly building units that have different types of external force–specific functional segments. Table 9-1 has more of them

TABLE 1-10. Collection of the self-assembly building units that have the combination of attractive (A), repulsive (R), and asymmetric packing (AP) segments. b and c indicate biological and colloidal building units, respectively.

Name	Kind	Group
1,2-dipalmitoyl-*L*-α-phosphatidylcholine (DPPC)	b	lipid
1,2-dimyristoyl-*L*-α-phosphatidylcholine (DMPC)	b	lipid
1,2-dioleoyl-*L*-α-phosphatidylcholine (DOPC)	b	lipid
1,2-dibehenoyl-*L*-α-phosphatidylcholine (DBPC)	b	lipid
1,2-dipalmitoyl-*L*-α-phosphatidylethanolamine (DPPE)	b	lipid
1-palmitoyl-2-oleoyl-*L*-α-phosphatidylcholine (POPC)	b	lipid
asymmetric gold nanorod (with surface charge)	c	
hemicylindrical plate with attached catalyst[1]	c	

[1] Ismagilov et al., 2002.

TABLE 1-11. Collection of the self-assembly building units that have the combination of attractive (A), repulsive (R), directional (D), and asymmetric packing (AP) segments. m, b, and b-m indicate molecular, biological, and bio-mimetic building units, respectively; n is an alkyl chain length, and the most common ones are shown for each homologue series.

Name	Kind	Group
octadecanamide, *N*-[4-(-β-*D*-glucopyranosyloxy)phenyl]-	m, b-m	
N-octadecanoyl-β-*D*-glucopyranosylamine	m, b-m	
N-dodecyl-*L*-gluconamide	m, b-m	
alkyl-β-*D*-glucoside (n = octyl - octadecyl)	m, b-m	
alkyl-β-*D*-maltoside (n = octyl - octadecyl)	m, b-m	
sodium cholate[a]	b	
sodium deoxycholate[a]	b	
cholic acid[a]	b	
deoxycholic acid[a]	b	
facial amphiphiles[b]	b, b-m	
1-palmitoyl-2-oleoyl-*L*-α-phosphatidylethanolamine (POPE)	b	lipid
collagen monomer	b	protein
bovine serum albumin	b	protein
adhesive protein mixture, *lustrin A*-based	b	protein
chitosan	b	protein
caseins	b	protein
alamethicin	b	peptide

[a]These are typical examples of facial amphiphiles.
[b]Most of the natural (such as bile salts) and synthetic facial amphiphiles belong to this segment combination. For more about these amphiphiles, please see Marquis et al., 2009 and the references therein.

TABLE 1-12. Collection of the self-assembly building units that have the combination of attractive (A), directional (D), and asymmetric packing (AP) segments. b and b-m indicate biological and bio-mimetic building units, respectively; surf. is short for surfactant.

Name	Kind	Group
oleic acid	b	lipid
elaidic acid	b	lipid
linoleic acid	b	lipid
glycerol monooleate	b	lipid
glycerol monoelaidate	b	lipid
glycerol monolinoleate	b	lipid
phytantriol	b	lipid
oleylamine	b-m	
12-hydroxystearic acid	b	lipid
12-hydroxystearyl alcohol	b	lipid
11-eicosenyl alcohol	b	lipid
sodium *N*-lauroyl-*L*-glutamate	b-m	surf.
sorbitan ester (Span series)[a]	b-m	surf.

[a]It includes monododecanoate (Span 20), monohexadecanoate (Span 40), monooctadecanoate (Span 55 or 60), monooleate (Span 80), tridodecanoate (Span 25), trioctadecanoate (Span 65), and trioleate (Span 85).

with details. All of the different types of self-assembly building units, in principle, can be subject to external forces during their self-assembly (Chapter 8). However, those with the external force–specific functional segments become more specific and selective on each of the external forces. This is critical for the development of many functional nanotechnology systems and their practical applications. Chapters

TABLE 1-13. Collection of the self-assembly building units that have external force-specific functional segment (EF-F). m, p, c, and b indicate molecular, polymeric, colloidal, and biological building units, respectively. n is an alkyl chain length, and the most common ones are shown for each homologue series.

Name	Kind	Group
4,4′-bis[{10-(trimethylammonio)decyl}oxy]azobenzene	m	
4,4′-bis[{12-(trimethylammonio)dodecyl}oxy]azobenzene	m	
4,4′-bis[{16-(trimethylammonio)hexadecyl}oxy]azobenzene	m	
12,12′-dithiobis[dodecyltrimethylammonium]	m	
8-ferrocenyl-N,N,N-trimethyloctanaminium bromide	m	
alkyldimethylamine oxide (n = octyl - octadecyl)	m	
ω-ferroceniumyl alkanethiol (n = octyl - octadecyl)	m	
poly(*N*-isopropylacrylamide)	p	
kinesin	b	protein
microtubule	b	protein
DNA	b	
F_1-adenosine triphosphate synthase (F_1-ATPase)	b	protein
antibody: immunoglobulin (Ig)	b	protein
bacteriorhodopsins	b	protein
poly(*N*-isopropylacrylamide) hydrogel	p, c	
poly(acrylic acid) hydrogel	p, c	
iron oxide nanoparticle	c	
Dynabead: polystyrene bead with magnetic core (Dynal, Norway)	c	
Most of the building units that are shown in Table 9-1.		

9 and 10 have detailed principles on these issues and corresponding examples. Important criteria for the assignment of external force–specific functional segments and their proper interpretations are shown in Figures 12-2(a, b) and 14.4(e, g, h, i, j).

1.6. CONCLUDING REMARKS

If those LEGO parts that my son uses were to bond too strongly when they are assembled, he would be limited in the number of diverse action figures he can build. Building figures with LEGOs is possible because they are designed to have a couple of simple yet fundamental structures. Also, since they easily fit into each other and easily come apart, they can be assembled and disassembled as often as my son desires.

Let us imagine that self-assembly is just like that. There are a couple of basic parts, which can be an atom, molecule, a part of colloidal particle, a whole colloidal particle, or a polymer skeleton, and the interactions among them are weak and flexible. Then, their assembly can be achieved with a high degree of freedom. We will surely be able to construct a variety of self-assembly systems with a good deal of diversity and flexibility. This chapter showed that there are five basic parts of self-assembly building units (segmental analysis): three fundamental segments and two additional segments. And the rule that matters the most is the concept of force balance, which is governed by weak interactions. Therefore, not only assembly among the five segments but also their disassembly can be as flexible as assembling and disassembling the LEGO parts. Once we have self-assembly building units,

what is necessary for their self-assembly is the force balance between each segment within the self-assembly building units. This is established as the general rules between the five segments, which may suggest a practical computational method for self-assembly in the future.

Strong bonds such as the covalent bond or ionic bond are literally strong compared with weak interactions such as the van der Waals force or hydrophobic force. Strong bonds are site-specific, it takes high energy to break them, and, once they are broken, it is not easy to rebind them to restore the original bonds. On the contrary, weak interactions are not strong, and they are easily broken, but they are abundant, non-site-specific (except for the hydrogen bond, but it still is less site-specific than the covalent bond), and easy to rebind, and, once they are broken, it is easy to restore the original interactions. This is one of the key practical advantages of self-assembly when it is applied in modern technologies including nanotechnology, bionanotechnology, nanomedicine, and computer science (Alper, 2005; Kaewkamnerdpong et al., 2007; Pelesko, 2007; Whitesides and Boncheva, 2002; Zemb and Blume, 2007).

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2

Nanotechnology Systems

Nanoscale science and technology (*nanotechnology* hereafter) have their building units ranging from atomic to molecular and to colloidal scale and sometimes beyond the colloidal scale. (For the choice of the term *building unit* instead of *building block*, see the second paragraph of the introduction of Chapter 1. The term *building unit* includes any types of entities that can assemble into any types of nanotechnology systems.) A great number of nanosystems and nanoscale systems are the results of the sophisticated assembly of their building units. (These two terms are often used without any clear distinctions. *Nanosystems* are the systems [including certain types of materials, devices, and even machines] whose entire physical scales are within the nanorange, such as nanometer, nanoliter, or nanoNewton. On the other hand, *nanoscale* systems are the systems whose whole dimensions reach beyond the nanorange but their critical physical units or critical operations remain within the nanorange. For the sake of simplicity, both will be referred as *nanotechnology system* throughout the book.) Surprisingly, the rules that govern this assembly are not that complicated. The vectorial sum of the different modes of interactions between the building units determines the structures and properties of nanotechnology systems. Furthermore, most of the interactions are relatively weak (compared with covalent and ionic bonds) intermolecular and colloidal forces. These forces are mostly fragment or functional group specific rather than specific to an entire building unit. At the same time, they are flexible and work cooperatively just like those in biological and bio-mimic systems. This was also the very core concept of self-assembly as stated in the previous chapter. Therefore, this is the logical point where the concept of self-assembly systems meets the concept of nanotechnology systems.

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Now let us go back to the LEGO action figures from the previous chapter. My 10-year-old son keeps building a variety of action figures by assembling and disassembling those simple yet fundamental parts. But what I have found with even more surprise is what he does when he runs out of the parts that he wants to use. He wants to add something more on top of the action figures that he has already built or to build some entirely new ones. What he wants is simple. He wants to add more functions so he can make them more playful. The problem he often encounters is that, since he already used up all the specific types of parts, he simply does not have the parts anymore in his LEGO basket. Sometimes, the parts that he wants do not exist at all. It may be easy to say that he can just cut or carve out some area of the parts as necessary. But that turns out to be very difficult. Those parts are small, which means that they are not easy to handle one-by-one. They look soft, but actually they are quite hard. And more importantly, they are very elegant, which means that, when they are assembled with each other, the elegant structural matching between them is the most critical factor that has to be met. What my son does to overcome this problem is surprisingly easy. He figured out that, by simply combining different types of parts in the usual way, he can build new sets of LEGO parts. These new parts are not ones that already exist (supplied by the manufacturer); they are now bigger and sometimes look like a new action figure. But, in many cases, he is able to make them fit onto the action figures he has already built so he can finally build the action figures that he wants equipped with the functions that he planned. Now that he realizes that this is possible and can be so much fun, he brings all the parts, not only from the LEGO products but from all the other products that he has as well. He brings a large plastic square that has regular lines of grooves and holes to use as a platform for his newly built action figures. He brings action figures from other toys such as BIONICLE and STAR WARS (also from The LEGO Group, please see the references) to decorate them with new functions and make them more realistic. And he often brings a battery from his battery box to power them. It seems to me that all it takes is a "logical combination" to make this amazing thing happen. As long as the operations of assembling, disassembling, and reassembling are reversible, which means the assembling is not permanent, there are endless possibilities for my son to create new action figures with new functions.

The previous chapter showed the segmental analysis approach for self-assembly systems. It was based on the fact that different types and sizes of self-assembly building units can be analyzed in a systematic manner. There can be a limitless possibility for building self-assembly building units by performing a "logical combination" of the five segments. This chapter shows that the segmental analysis approach for self-assembly systems can be directly expanded for nanotechnology systems. This can be compared with building LEGO action figures, mentioned in the previous paragraph, almost in a parallel manner. If we are imaginative enough to see that building action figures by assembling existing LEGO parts is like building self-assembly systems by logically combining necessary segments, building new action figures with new functions by combining the existing parts with newly assembled parts (from the existing parts) can be viewed as building nanotechnology

systems by combining existing self-assembly building units with new building units that are assembled from the existing self-assembly building units. As will be shown throughout this chapter, most of the nanotechnology systems can be viewed as the result of the logical combination of different types of basic building units. Some of them are the self-assembly building units from the previous chapter and some of them are the new building units that can be assembled by combining the existing self-assembly building units with others. Three different types of building units will be described and named *nanoassembly building units*. The rules among them when they are "logically" combined will be discussed as well. One of the critical reasons that this approach to nanotechnology systems is possible comes from the fact that, just as with the self-assembly systems, the elegant balance between weak intermolecular and colloidal forces is the key to bringing the nanoassembly building units together. This is the case for a good part of the nanotechnology systems, which leads us to establish a general diagram for nanoassembly systems. We can greatly benefit from the fact that self-assembly and nanotechnology systems share the same working forces and the same building units.

2.1. NANOASSEMBLY

The previous chapter defined a self-assembly as a thermodynamic or kinetic assembly of its building units. All possible entities (atoms, molecules, colloidal particles, etc.) that can participate in this process are self-assembly building units. Building units for nanotechnology systems have more structural hierarchies. Nanotechnology systems can be built not only through self-assembly processes but through an external manipulation as well. All these efforts to create nanotechnology systems can be considered as the processes for assembling nanotechnology systems. We will define this as a *nanoassembly*, which can be stated as a "thermodynamic, kinetic, or manipulative assembly of nanoassembly building units." Spontaneous assembly of nanoassembly building units will be a great route for building nanotechnology systems. However, assembling them, for example, using an atomic force microscope through a one-by-one type of operation with any type of nanoassembly building units will also be a great alternative for creating nanotechnology systems.

Figure 2-1 (left-hand side) shows that nanoassembled systems are assembled from three basic nanoassembly building units. (The definition of nanoassembled system and the relation with nanotechnology system will be presented in the sixth section of this chapter.) They are a self-assembly building unit, a fabrication building unit, and a reactive building unit. As will be described in the next section with more details, the structures of all three basic nanoassembly building units can be analyzed based on the concept of segmental analysis. In other words, the segmental analysis that was developed for self-assembly building units can be expanded for the two other types of building units. Figure 2-2 explains this. All three basic nanoassembly building units can be analyzed with the three fundamental and two additional segments. And all segments from the three basic nanoassembly building units interact through the force balance with any possible combinations. The whole

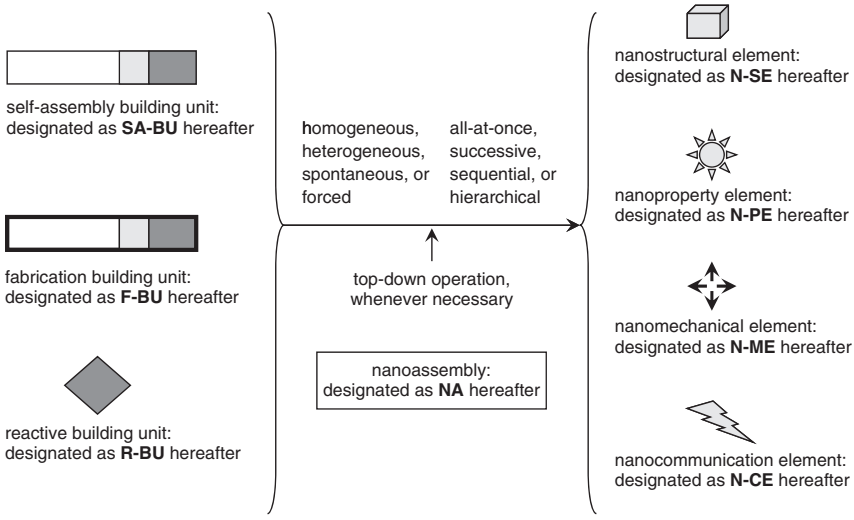


Figure 2-1. Three basic nanoassembly building units construct the four nanoelements. Force balance between the nanoassembly building units plays a key role.

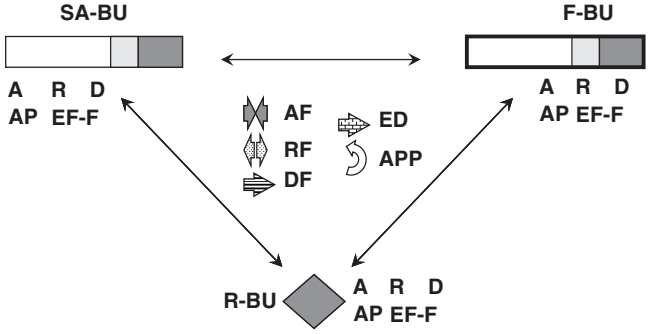


Figure 2-2. The fundamental and additional segments of self-assembly building unit (**SA-BU**), fabrication building unit (**F-BU**), and reactive building unit (**R-BU**) can interact through the force balance with any possible combinations. **AF, RF**, and **DF** represent attractive force between **A**s, repulsive force between **R**s, and directional force between **D**s, respectively. **A, R, D, AP**, and **EF-F** refer to attractive, repulsive, directional, asymmetric packing, and external force–specific functional segments, respectively. **ED** is external force–induced directional factor. **APP** is asymmetric packing process.

process resembles the self-assembly process. But it now occurs in a "*quasi*-three-dimensional" way, which is to imply that there are three different types of building units instead of just one (as for self-assembly).

The concept of force balance is directly applied not only between self-assembly building units, between fabrication building units, or between reactive building units, but between all three different types of building units as well. This gives us an

important insight for the third part of this book that there can be great possibilities for building nanoassembled systems once the three basic building units are well identified and the relationships between them are well controlled. The roles of the five segments during the assemblies of nanoassembled systems are the same as for the assemblies of self-assembled systems.

2.2. IDENTIFICATION OF BUILDING UNITS

2.2.1. What Is a Nanoassembly Building Unit?

Let us now define nanoassembly building units with more details. As described in the previous section, there are three different types of basic building units for nanoassembled systems. Any possible "logical" or even "random" (as long as it makes sense as a nanoassembled system in the end) combinations of any building units regardless of their sizes and types can be imagined to assemble nanoassembled systems. They may be assembled through the combination of only one type of nanoassembly building units. They may be with two different types of building units or with all three types. They are assembled through one route of (or combined routes out of) the four different major routes: homogeneous, heterogeneous, spontaneous, and forced routes. There are also four different assembly modes: all-at-once, successive, sequential, and hierarchical. The four routes and the four modes are always correlated in a combinatorial way. Therefore, there are 16 different kinds of assembly processes for nanoassembly building units. Whenever necessary, top-down operations can be used during assembly processes. Details will be presented throughout the third part of the book.

Table 2-1 presents representative examples of the three basic nanoassembly building units. A self-assembly building unit is all possible combinations of the three fundamental and two additional segments (Figures 1-3 and 1-5). It also includes any objects that can be under force balancing by any of the physical, chemical, or conditional factors (Tables 1-1 and 1-2). A fabrication building unit covers the building units that are evolved one step further from the self-assembly building units. Typical fabrication building units are the objects that are composed of two or more self-assembly building units. Mostly, this is obtained by self-assembly. Some examples are shown in the table. A fabrication building unit also includes any objects that are fabricated by top-down or bottom-up/top-down hybrid approaches. As shown in the table, this fabrication building unit can be a part of a solid substrate or solid substrate itself. It can also be a part of the bulk material from which a nanoscale structure is built or carved out. Often, there is a nanoassembly system in which the solid substrate that is nanostructured with a top-down method should be viewed as a self-assembly building unit in order to understand the nanoassembly process more logically. This case will be discussed in the third part of the book whenever necessary. Reactive building units possess the possibility of reaction between themselves or with other nanoassembly building units. Examples include inorganic precursor, intermediate precursor, atomic or molecular beam, decomposable organometallic substance, and reactive monomer.

TABLE 2-1. Representative examples of the three basic nanoassembly building units. SA-BU, F-BU, and R-BU refer to self-assembly, fabrication, and reactive building units, respectively.

SA-BU	all possible combinations of fundamental and additional segments for self-assembly any object that can be under force balancing by physical, chemical, or conditional factors
F-BU	any object that is composed of more than two **SA-BU**s mostly by self-assembly *for example:* self-assembled monolayer-covered metal surface organic monolayer-protected nanocluster surface-decorated carbon nanotube any object that is fabricated by top-down or bottom-up/top-down hybrid operation *for example:* lithographically patterned solid surface dip-pen written/patterned organic layer on solid surface etched solid nanostructure
R-BU	inorganic precursor intermediate precursor atomic or molecular beam decomposable organometallic substance reactive monomer

2.2.2. Fabrication Building Units

A fabrication building unit can be obtained through different routes. Figure 2-3 shows some typical examples. First, a self-assembly building unit can self-assemble with another self-assembly building unit. This produces the most abundant type of fabrication building unit, which can possess the characteristics of both self-assembly building units. One of the typical examples is the nanocluster whose surface is protected with a functional organic layer. One reason to have a fabrication building unit of this type is that, in many cases, it can ensure an improved nanoassembly process. This can be especially the case when one-by-one assembly of each self-assembly building unit becomes problematic. Very often, it is not easy to assemble nanoclusters into desired nanostructures when they do not have enough repulsive force to counterbalance the attractive force. Modifying the surface of the nanocluster with proper organic molecules having long hydrocarbon chains can be a practical method to provide a necessary steric repulsion. At the same time, the organic molecule can be used as a modifier to control the structure and property of the nanoassembled system.

A fabrication building unit can also be obtained through the combination of a self-assembly building unit with a substrate that will be eventually assembled into a nanoassembled system. Furthermore, any types of plain substrates that are structured by physical, chemical, or mechanical means can be considered fabrication building units. This stands valid as long as they become part of a nanoassembled system and as long as the structured parts (pore, channel, groove, or layer) induce an improved capability for the nanoassembly. For some of the structured substrates, this effect becomes relatively less significant than for the substrates that are combined with self-assembly building units. When this is the case, it is

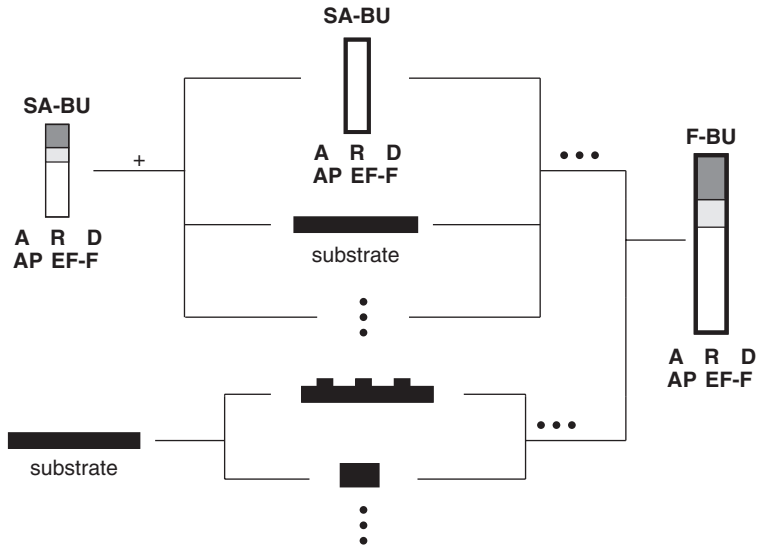


Figure 2-3. Typical routes for the preparation of fabrication building units (**F-BU**). **A, R, D, AP**, and **EF-F** refer to attractive, repulsive, directional, asymmetric packing, and external force–specific functional segments, respectively. **SA-BU** is self-assembly building unit.

more realistic and practical to treat the structured substrates as a self-assembly building unit. Figures 12-2(d) and 14-4(f) will show some representative examples for the structured substrates that are self-assembly building units. Plain substrates (substrates that are not structured) are self-assembly building units whenever they become a part of the nanoassembled system. Figures 11-2(c) and 12-2(d) provide some examples for this case. When substrates simply support self-assembly building units or any other objects, they are just substrates. On the contrary, when substrates are chemically modified in order to achieve an improved nanoassembly capability, it becomes more convenient to treat them as fabrication building units. Figure 11-2(d) will show a good example of this.

As indicated at the right-hand side of Figure 2-3, whatever route has been taken to obtain a fabrication building unit, the concepts of the three fundamental segments and the two additional segments are directly valid for it. Once a fabrication building unit has been obtained, exactly the same segmental analysis (as for self-assembly building units) can be performed for the fabrication building units. Each fabrication building unit has its own segmental combination. It is simply because, as stated before, the working forces between fabrication building units are exactly the same weak intermolecular or colloidal forces as for self-assembly. Their working-length scale is also the same. A unified view that explains the stability of the gold nanoparticle whose surface is modified with self-assembled thiolates or phosphines (which makes the gold nanoparticle a fabrication building unit in terms of the definition presented in this section) by using the noble-gas superatom analogy will be good reading material in this regard (Walter et al., 2008).

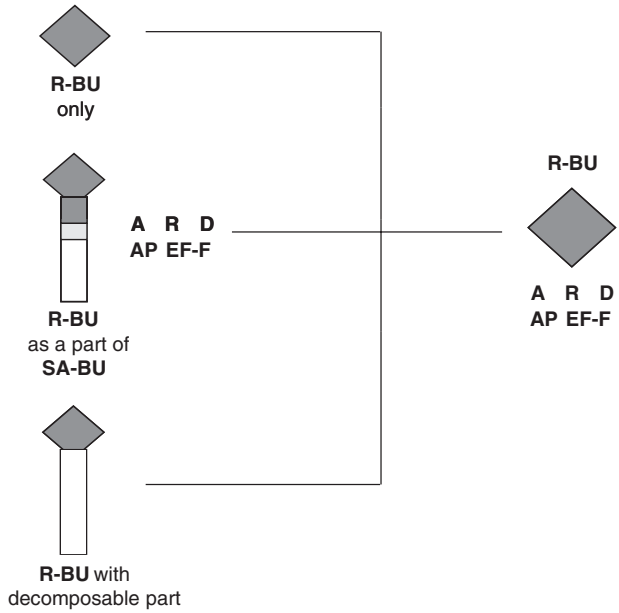


Figure 2-4. Different types of reactive building units (**R-BU**). **A, R, D, AP**, and **EF-F** refer to attractive, repulsive, directional, asymmetric packing, and external force–specific functional segments, respectively. **SA-BU** is self-assembly building unit.

2.2.3. Reactive Building Units

Reactive building units are not obtained through self-assembly. Mostly, they exist already or can be synthesized by rational design. Figure 2-4 presents three different types of reactive building units. The first type has only a reactive part. Many simple precursors belong to this one. A whole part of this building unit undergoes at least some degree of reaction when it assembles with other nanoassembly building units. The second type is the one whose reactive part is a part of a self-assembly building unit. Only the reactive part participates in the reactive interaction with other nanoassembly building units while the other part interacts through force balancing. The third type is the reactive building unit that has a reactive part along with a decomposable part. The reactive part becomes a part of a reactive nanoassembly. But the difference from the second type is in its decomposable part. At the beginning of nanoassembly, this part participates as a part of a nanoassembly process (as one of the segments), thus playing a significant role in it. But once the nanoassembly is completed (or during the process), this part is decomposed out. The final nanoassembled system does not retain this part. Most of the metalorganic chemical vapor deposition (MOCVD) precursors belong to this type of reactive building unit.

Regardless of the type, the concept of segmental analysis is directly valid for the reactive building units. Throughout the book, all three types of reactive building units will be referred to as a reactive building unit with the symbol of a filled diamond. But every single reactive building unit, just like self-assembly and

fabrication building units, has its own segmental combination. This fact will be readdressed throughout the third part of the book whenever necessary.

2.3. NANOELEMENTS

Figure 2-1 showed that nanoassembled systems are obtained through nanoassembly with three basic nanoassembly building units. Nanoassembled systems can have a diverse range of structures and physical/chemical properties and diverse functional properties. For many nanoassembled systems, these general properties are those that are already known to other existing systems such as macroscopic counterparts. They can be directly characterized. However, for many others, they can be novel properties that cannot be easily recognized and characterized. There are also nanoassembled systems whose general properties are overlapped by others.

The concept of force balance for nanoassembly makes it possible for us to evaluate the specific properties that can be expected from certain nanoassembly building units. As will be shown in the third part of the book, it can provide a nice insight when choosing a proper nanoassembly route for a specific nanoassembled system and help clarify intended nanoscale properties (or nanoproperties) with a reasonable degree of accuracy. Four elemental properties (which will be called *nanoelements* hereafter) for nanoassembled systems are proposed here in order to address these properties in a systematic manner. They are nanostructural element, nanoproperty element, nanomechanical element, and nanocommunication element. The symbols for each nanoelement are also shown in Figure 2-1.

Table 2-2 shows representative examples of the four nanoelements. A nanostructural element is the structural features that are inherited or designed

TABLE 2-2. Representative examples of the four nanoelements. N-SE, N-PE, N-ME, and N-CE refer to nanostructural, nanoproperty, nanomechanical, and nanocommunication elements, respectively.

N-SE	nanoparticle	**N-ME**	gating and switching
	nanopore		rotation and oscillation
	nanofilm		shafting, shuttling, and elevatoring,
	nanotube		contraction-and-extension
	nanorod		walking
	nano hollow sphere		tweezering and fingering
	nanofabricated surface		rolling and bearing
			pistoning, sliding, and conveyoring
N-PE	surface plasmon		self-directional movement
	quantum size effect		capture-and-release
	melting point depression		sensoring
	capillary condensation		directional flow
	single electron tunneling		
	surface catalytic activity	**N-CE**	any macroscale performance that is shown by nanointegrated system
	mechanical strength		any macroscale signal exchange (electric, magnetic, or optical) and energy exchange that are performed by nanomachines
	energy conversion		
	conductivity transition		
	nano-confinement effect		
	tensile strength		

from nanoassembly itself. As shown in the table, most of the nanostructure-based nanoassembled systems belong to this. A nanoproperty element is the properties that are inherited, induced, or designed from nanoassembly and its framework. Some of them could be the same properties as macroscale counterparts but in the nanoscale while others are those that emerge only when the systems have nanoscale features. A nanomechanical element is the unit operations (for details, see Lee, 2008) that are designed to express the motional aspects of nanoassembled systems. Shown is 12 representative unit operations, but there certainly could be more as nanotechnology progresses. Finally, a nanocommunication element is a signal, energy, or work that is designed to communicate with the macroworld. This nanoelement is almost exclusively for nanofabricated systems, nanointegrated systems, nanodevices, and nanomachines. Details about them will be described in the sixth section of this chapter.

2.4. IMPLICATION OF BUILDING UNIT STRUCTURES FOR NANOASSEMBLIES

The previous sections showed that the same segmental analysis for self-assembly building units is valid for nanoassembly building units and that the same concept of force balance is applied for their interaction to produce nanoassembled systems. This helps establish general rules among nanoassembly building units. These rules then allow us to grasp the general tendency of different nanoassemblies.

Figure 2-5 presents the general rules among nanoassembly building units. Its appearance is almost identical to Figure 1-6. As in Figure 1-6, we begin with the point of initial force balance (designated as a filled circle). Let us assume that we have a well-known nanoassembly system whose building units have clearly analyzed attractive and repulsive segments. We thus know that this system will be assembled at a given condition through the balance between attractive and repulsive forces. Any nanoassembly system that can satisfy this prerequisite can be set as the point of initial force balance. In other words, it can be used as a starting point for the tracking of other nanoassembly systems.

First, the horizontal arrow is for the nanoassembly systems whose force balance is achieved only through attractive and repulsive segments. This will be always the case regardless of the types of nanoassembly building units. Whether the nanoassembly is between the same type of building units (for example, fabrication building units) or between different types of building units (for example, fabrication building unit with self-assembly building unit), it can be tracked along this arrow as long as all building units have only attractive and repulsive segments. If the segmental analysis shows the increase of the attractive interaction between them while the repulsive interaction remains the same, the nanoassembly will occur in a more favorable way (toward the right-hand side). The common self-assembly parameters such as *cmc* (critical micellar concentration), *can* (critical aggregation number), and aggregation number cannot be very useful for the evaluation of the favorability of nanoassembly here. Since nanoassembly usually occurs with different types

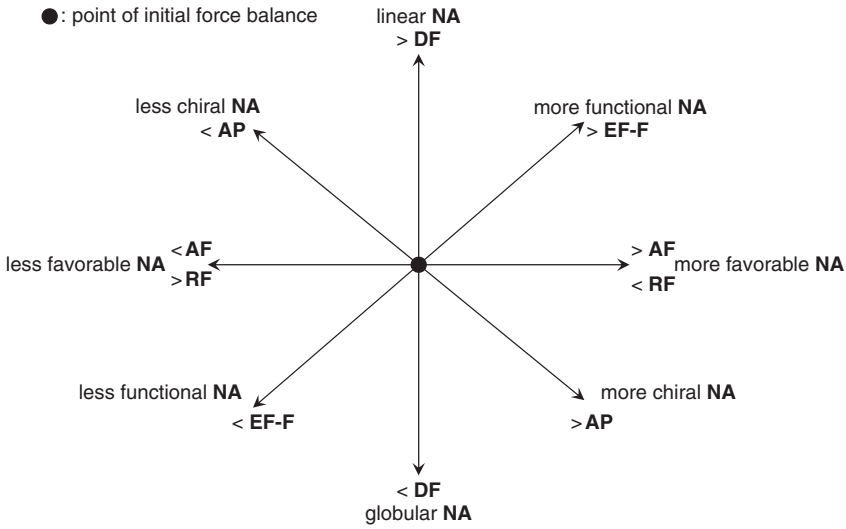


Figure 2-5. General rules between the nanoassembly building units. **NA** is short for nanoassembly. **AF, RF**, and **DF** refer to attractive, repulsive, and directional forces, respectively. **AP** and **EF-F** are short for asymmetric packing and external force–specific functional segments, respectively.

of building units, its favorability can be determined rather by the observation of its outcome (or yield). There can be some nanoassembly systems whose favorability can be judged by self-assembly parameters, especially when the building units are only self-assembly building units. But, in most cases, measuring the amount of the nanoassembly building units that are nanoassembled and comparing it with the total amount of the building units that are put into the system initially can provide a good sense of its favorability. Nanoassembly will also be a favorable process when the repulsive interaction between the building units is decreased while the attractive interaction remains the same. If the segmental analysis shows the increase of the attractive interaction while the repulsive interaction is decreased, the nanoassembly will be even more favorable. The direction toward the left-hand side of this arrow is exactly the opposite case. When the attractive interaction is decreased while the repulsive interaction remains the same, the nanoassembly will be less favorable. When the repulsive interaction is increased while the attractive interaction remains the same, the nanoassembly will also be less favorable. And when the attractive interaction is decreased while the repulsive interaction is increased, the nanoassembly will be even less favorable. Less favorable assembly does not necessarily mean that there will be no nanoassembled system. It simply means that the outcome (or yield) will be less than the one at the point of initial force balance. As the ratio of the attractive interaction to the repulsive interaction is decreased, there will be less and less nanoassembled system assembled. When the system reaches the point of total dominance of the repulsive interaction over the attractive interaction, there will be no more nanoassembled system or its amount becomes negligible.

As in Figure 1-6, the vertical arrow is for the directional interaction. As a directional interaction is induced between any nanoassembly building units, the nanoassembly process will experience some degree of directionality. The more directional interaction means the more directional nanoassembly, which is the upward direction on the vertical arrow. Usually, this linear nanoassembly generates a nanoassembled system with a less globular structure. In some cases, it helps create a nanoassembled system with a film form including multilayer, bilayer, or even monolayer. This may look like an extreme case, but actually it is an abundant case of nanoassembly, which has an important technological implication. The downward direction of this arrow means a less directional interaction. There can be some different segmental conditions that fit in this direction. The most likely case is the nanoassembly system that has a directional segment whose directional interaction is significantly disrupted by other factors. This disruption could be caused by an intrinsic reason or by an external force whenever it enforces the attractive or repulsive interaction that works against the directional interaction. In some cases, the nanoassembly system with no directional segment can be in the situation where the force balance between the attractive and repulsive segments is disrupted by the directional interaction caused by an external force. Whatever the actual cause is, the nanoassembly toward this direction generates a nanoassembled system with a less linear (more globular-like) structure. More disruption results in less organized nanoassembled systems. The result of nanoassembly along this vertical arrow cannot be judged by the conventional self-assembly parameters unless the only nanoassembly building units that are involved are self-assembly building units. As with the attractive interaction–repulsive interaction balance line (horizontal arrow), it usually can be determined by the outcome (or yield) of the nanoassembled system or, especially in this case, by the geometry of the nanoassembled system. It will be quite safe to say that less three-dimensionality is the result of more involvement of the directional interaction.

The same general rules are valid for functional and chiral nanoassemblies. When a nanoassembly building unit has an external force–specific functional segment, the nanoassembled system will have a strong possibility of having a functionality that is specific on the external force. Just because there is an external force–specific functional segment, it does not automatically become a more favorable nanoassembly. Depending on the force balance condition, it can be actually less favorable, particularly if the functional segment works against the initial force balance between the attractive and repulsive segments. This is when the nanoassembly process follows the downward direction of the diagonal arrow. A similar explanation can be given for chiral nanoassembly. If a nanoassembly building unit has an asymmetric packing segment, the nanoassembly more likely occurs in a chiral manner. It might have multiple steps of process whose actual assembly direction could be quite diverse and subsequently the nanoassembled system could have a lot more variety of morphologies and sizes. And just because there is an asymmetric packing segment, it does not necessarily mean that the nanoassembly will be more favorable than the one at the point of initial force balance. As it happens occasionally, the asymmetric packing cooperating with the balancing between the attractive and repulsive

forces can make the whole force balance lag behind (happen later) compared with the nanoassembly system without any asymmetric packing segment. When this is the case, the upward direction on the arrow should be followed to track the nanoassembly process.

As will be shown in the third part of the book, the functional and chiral nanoassemblies are particularly important for the development of many practical nanotechnology systems that require mechanical and communication nanoelements. A surprisingly diverse range of these nanoelements can be explored by taking advantage of the characteristics of the functional and chiral nanoassemblies.

2.5. GENERAL ASSEMBLY DIAGRAM

The general tendency of nanoassembly can be established by using the general rules between nanoassembly building units from the previous section. This will have a phase diagram type of appearance and function as in Figures 1-7 and 1-8. Moreover, it should be this way considering the repeatedly described facts that the fundamental driving forces and building units are the same for both self-assembly and nanoassembly systems. Each nanoassembly system has some degree of variation and unique characteristics of its own, which might not allow us to follow the exact nanoassembly process using this diagram. However, this diagram can be used to follow nanoassembly processes and as a starting point for the prediction of the outcome of nanoassembly. It is useful over a wide range of nanoassembled systems with reasonable accuracy.

Figure 2-6 shows the general tendency of nanoassembly. As Figure 2-5 (for nanoassembly building units) was constructed from Figure 1-6 (for self-assembly building units), Figure 2-6 is built on Figure 1-7. Some details for the different types of nanoassemblies were described in Figure 2-1. More details for each type of nanoassemblies will be presented in Chapters 7 and 8. To briefly explain them, first, nanoassembly can be classified into two main processes: *homogeneous* and *heterogeneous* nanoassemblies. The former is the nanoassembly only between the same types of nanoassembly building units while the latter is the one between the different types of nanoassembly building units. For example, if the nanoassembled system is assembled only from self-assembly building units or only from fabrication building units, it is a homogeneous nanoassembly. On the other hand, if the nanoassembled system is assembled from a self-assembly building unit with a fabrication building unit, it is now a heterogeneous nanoassembly. For some systems, this classification may not appear logical, since some fabrication building units look like self-assembly building units. However, for most of the nanoassembly systems, when it comes to the stage of selecting the right nanoassembly building units and the right nanoassembly route for them, this classification can give us a practical means to start. Chapter 7 has the full description for this issue. Second, nanoassembly can be divided into *spontaneous* and *forced* nanoassemblies. The former is the nanoassembly whose building units acquire their force balance without the aid of external force. The latter is the opposite case. Forced nanoassembly is

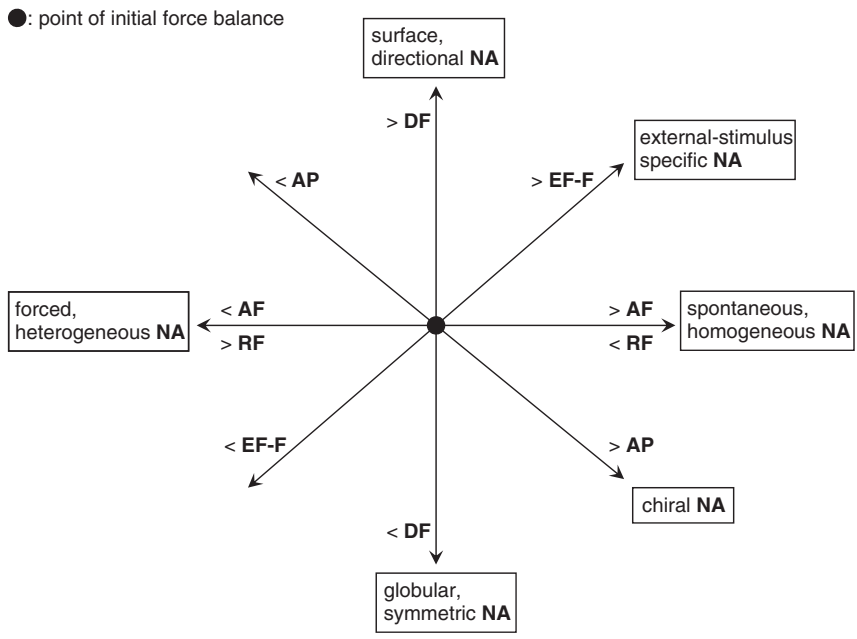


Figure 2-6. General tendency of the different types of nanoassemblies. **NA** is short for nanoassembly. **AF, RF**, and **DF** refer to attractive, repulsive, and directional forces, respectively. **AP** and **EF-F** are short for asymmetric packing and external force–specific functional segments, respectively.

the nanoassembly whose building units cannot acquire the force balance by themselves, which means that they cannot assemble without an external aid, thereby requiring a well-designed external force to achieve the nanoassembly. Chapter 8 has the details. Surface and directional nanoassemblies are on the opposite side of globular and symmetric nanoassemblies. Thus, the symmetric nanoassembly here implies that the surface and directional nanoassemblies are not symmetric, which in a practical manner means that the surface and directional nanoassemblies occur with less symmetry than globular nanoassembly. Chiral and external-stimulus-specific nanoassemblies are those with an asymmetric packing segment and an external force–specific functional segment, respectively.

The horizontal arrow explains homogeneous and heterogeneous nanoassemblies along with spontaneous and forced ones. Let us assume that the point of initial force balance is set up nicely by using a well-established nanoassembly system. And let us assume that the segmental analysis of another system that is under study shows that the attractive interaction between its building units is increased while the repulsive interaction remains the same. As can be predicted from Figure 2-5, this will trigger a more favorable nanoassembly compared with the one at the point of initial force balance. As also discussed in Figure 2-5, there can be other segmental situations that can result in the same tendency of nanoassembly. Many homogeneous nanoassembly systems have their nanoassembly processes occurring

toward the right-hand side of the arrow and spontaneously. This is because, when a nanoassembly system has the same types of building units, there is a reasonable possibility that the building units can be force balanced without any intervention of external force. When a system begins to move toward the opposite direction (left-hand side), it is obvious from Figure 2-5 that the repulsive interaction overcomes the attractive interaction. Details for this direction were described in Figure 2-5. As long as the building units acquire the force balance without any external force, some heterogeneous nanoassemblies can be spontaneous, too. However, for many heterogeneous nanoassemblies, especially when the building units have more different types and more diverse morphologies, it becomes more likely that they cannot acquire the force balance by themselves. A proper external force has to be selected and applied to obtain the nanoassembled system.

Now let us take a look at the vertical arrow. This is for the directional interaction. Most of the nanoassemblies that occur on the surface of any type of substrate, whether it is intended that way or not, become the directional nanoassembly. This is simply because the interaction of nanoassembly building units with the substrate, in most cases, generates the force that is acting along the direction of the surface of that particular substrate. More directionality means moving upward along the vertical arrow. When the situation of building units changes to moving downward, which means that the nanoassembly occurs with less or disrupted directional interaction, the nanoassembled system becomes globular and less organized.

Nanoassemblies with an external force–specific functional segment and an asymmetric packing segment can provide quite an advantage for the assembly of nanoassembled systems that are functional. A tracking of individual nanoassembly process on the two diagonal arrows is the same as in Figure 2-5.

The outcome of self-assembly is self-assembled aggregate. For nanoassembly, it goes one step further. The apparent initial outcome of nanoassembly is a nanoassembled system. But it is the nanoelements (Figure 2-1 and Table 2-2) that make nanoassembled systems distinctive from self-assembled aggregates. Self-assembled aggregates have their own characteristic properties, which in many ways are useful, and many applications have been established using them over a wide range of scientific and technological fields. For nanoassembled systems, it is the nanoelements that define their characteristic properties, and with which we are seeking practical applications for nanotechnology systems.

Figure 2-7 presents the general rules of nanoassembly and their relationship with nanoelements. Representative examples will be given in the third part of the book. As a nanoassembly becomes more favorable (moving toward the right-hand direction on the horizontal arrow of attractive interaction–repulsive interaction balance), it is more likely that the nanoelement that will be expressed is a nanostructural element. Typical nanopores, nanoparticles, nanocrystals, nanoemulsions, and nanocomposites are more likely to be obtained on this side of the arrow. On the other hand, if a nanoassembly moves toward the left-hand side, it is more likely to obtain nanoassembled systems that usually need an aid of external force for their assembly. Colloidal crystal is one good example, especially when the

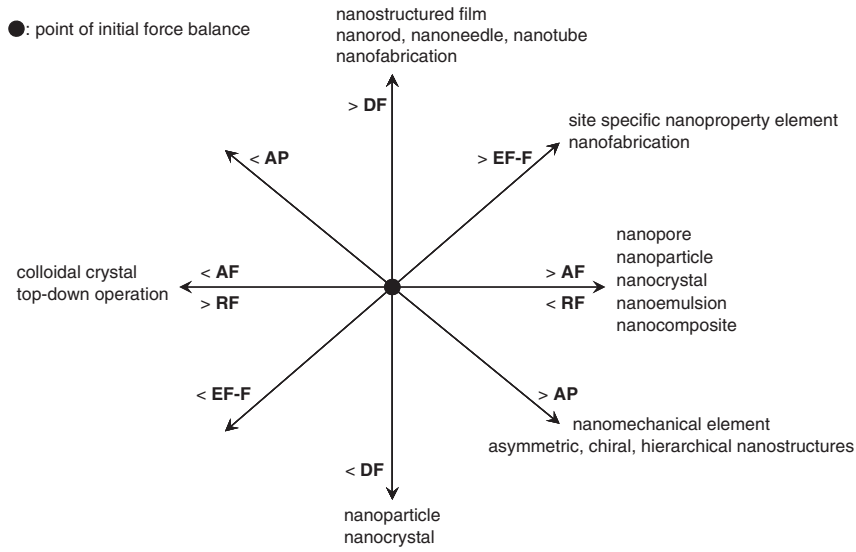


Figure 2-7. General rules of nanoassembly and different types of nanoelements. **AF, RF**, and **DF** refer to attractive, repulsive, and directional forces, respectively. **AP** and **EF-F** are short for asymmetric packing and external force–specific functional segments, respectively.

size of nanoassembly building unit (colloidal particle) is increased. Many top-down operation-based nanoelements are other examples. When a nanoassembly is involved with a directional interaction, the most likely nanoelement will be a film or surface-based nanoscale operation. Examples include most of the nanostructured films regardless of their detailed morphology. Nanoporous film, nanolayered film, and nanopatterned film are among them. It also includes most of the nanoscale products that are obtained as a result of directional growth (from the spherical-shape) such as nanorods, nanoneedles, and nanotubes. A good deal of nanofabrication is basically the nanoscale process that is performed on the surface, and thus becomes one prominent example for the upward direction on the vertical arrow. The opposite direction produces nanoelements, too. Some nanoparticles and nanocrystals can be obtained at this end. Most of the nanoproperty elements come along with nanostructural elements. And they are coupled to each other in many ways. Most of the nanoproperty elements originate because the nanostructural elements are in the nanoscale. And the changes in nanoproperty elements can be practical because the changes in nanostructural elements are practical through nanoassembly. Chapters 11 and 12 have the details for this.

The nanoassemblies that occur with external force–specific functional and asymmetric packing segments are critical for nanomechanical and nanocommunication elements. As shown in the figure, they are also vital for site-specific nanoproperty elements. Electron tunneling and Coulomb blockade are good examples. Nanofabrication can take advantage of the unique features of external stimulus–specific nanoassembly, too. For a chiral nanoassembly, the chirality that is unique on each

system can be used for the development of the nanostructures that can take advantage of the uniqueness, which includes highly asymmetric nanostructures, chiral nanoparticles, and some hierarchically constructed multiple-length-scale nanomaterials. It is also important for many unique types of nanomechanical elements. By coupling with the external stimulus–specific nanoassembly, the development of nanoelements on this side (right-hand side of both external stimulus-specific and chiral nanoassemblies) can be much more fruitful. As far as the application for nanotechnology systems goes, the other side (left-hand side) of both diagonal arrows does not have much use in the development of specific nanoelements.

Figure 2-8 shows a conceptual universal diagram for nanoassembly. A practical following of nanoassembly processes can be done using this diagram. Its appearance is almost identical to the one for self-assembly in Figure 1-8. Since nanoassembly is involved with three different types of building units, the nanoassembly system that is designed to occur via more a favorable route can have a lot more advantages than the one having less favorability, which might need the aid of external force to be properly assembled. Of course, the external force–induced nanoassembly is an important part of the whole nanoassembly family. But if a nanoassembly can be successfully performed without aid of external force, which means spontaneously, it may be a wise choice not to use an external force unless there is an obvious advantage or absolute necessity to use it. This is one reason that when it comes to designing a nanoassembly system, it is usually the right-hand side of the diagram that can bring a better outcome. A better outcome can be judged by the simplicity of the nanoassembly process and more yield. It is ultimately the nanoassembled

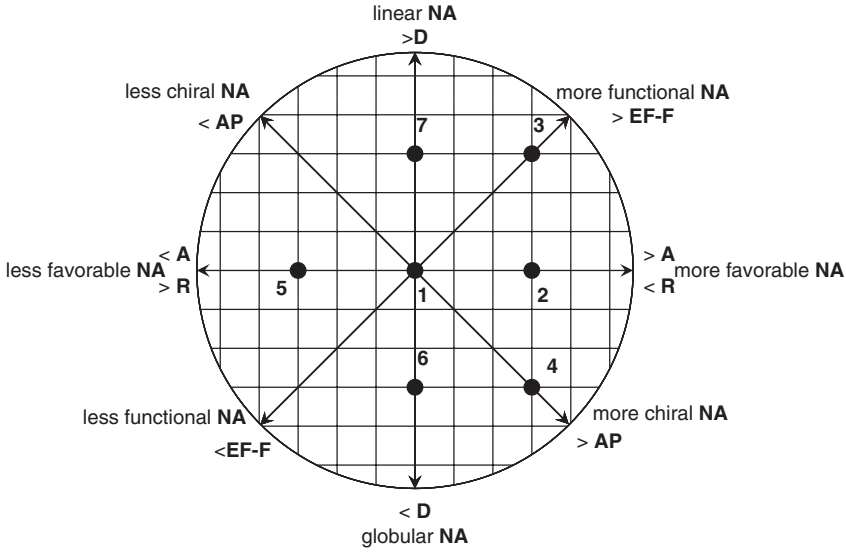


Figure 2-8. Conceptual universal diagram for nanoassembly (**NA**). **A, R, D, AP**, and **EF-F** refer to attractive, repulsive, directional, asymmetric packing, and external force–specific functional segments, respectively.

products that we are aiming for, which brings the issue of productivity. However, this should not, by any means, denounce the importance of external forces in many nanoassembly processes. They can dramatically increase the scope of nanoassembly systems we can explore. They can also help assemble certain types of nanoassembly building units effectively, which otherwise would not be possible.

As in Figure 1-8 for self-assembly, the first step is finding out the point of initial force balance: point 1. This can be done with a reference nanoassembly system. Let us assume that we have a well-known nanoassembly system whose building unit is composed of only one attractive segment and one repulsive segment. The difference from the universal diagram for self-assembly is that these attractive and repulsive segments need not be from just one type of building unit but can be from different types of building units. However, as long as the segmental analysis is properly performed, which means that we have a clear idea which part of the building unit will play as what type of segment with what degree of magnitude, strength, and spatial effect, the fundamental logic remains exactly the same as that for self-assembly. If they satisfy any one of the segmental conditions for favorable nanoassembly, the nanoassembly process will occur spontaneously. Now let us move to point 2. It is for the nanoassembly system that has increased attractive interaction or a higher ratio of an attractive interaction to a repulsive interaction. Simply, this system will be assembled more favorably than the one at point 1. The nanoassembled system will have a higher possibility having a better yield and possibly being more organized. This will be pretty much the case even if there are additional building units compared with the one at point 1, which means that there are more attractive segments from different types of building units. All that matters is the force balance between them. The more total attractive interaction should result in the more favorable nanoassembly regardless of the numbers and types of building units. On the opposite side of nanoassembly, if a nanoassembly system under consideration turns out to have less attractive interaction or a smaller ratio of an attractive interaction to a repulsive interaction compared with the one at point 1, we now have a system that will be assembled less favorably than the one at point 1. Point 5 is for this situation. As long as there are enough interactions between the segments to satisfy the force balance, there will be a nanoassembled system. But the yield will be lower than that of points 1 and 2, and there will be a good chance that the nanoassembled system will be less organized. This is one typical situation when the aid of external force should be considered to possibly increase the yield and integrity of the nanoassembled system.

Now let us take a look at points 6 and 7. They are for the nanoassembly systems with a directional interaction. Point 7 is for the system with more directional interaction than the one at point 1. Point 6 is with less directional interaction. A linear type of nanoassembled system such as film will be most likely obtained from the system at point 7. Its yield will be mostly higher than that obtained without any directional interaction. For the nanoassembly system at point 6, it will be a safe argument to make that its nanoassembly will be less directional than the one at point 7 and its nanoassembled system will be less organized with much less yield than the ones at point 7 and at point 1. One important fact here is that, for

many nanoassembly systems, the directional interaction most likely originates from external forces rather than intrinsic factors. For self-assembly systems, it is mostly from intrinsic factors.

Lastly, points 3 and 4 are for the nanoassembly systems whose building units have an external force–specific functional segment and an asymmetric packing segment, respectively. For the purpose of clarity, that is, just to make the explanation simple, let us assume that the segmental structure of the system at point 3 is exactly the same as the one at point 2 except that it has an external force–specific functional segment. Then, the following of its nanoassembly process begins from point 2. The system at point 3 will be a favorable nanoassembly as much as the one at point 2. And it now will be a functional one, which means that the nanoassembled system has a specifically designed nanoscale function. Whereas, if we assume that the nanoassembly system under consideration has an asymmetric packing segment and the rest of the segmental structure is exactly the same as the one at point 2, it now will be a chiral nanoassembly. Point 4 represents this situation. Like the one at point 3, this has technological importance for the development of nanomechanical elements that could be incorporated into a wide range of nanodevices.

Almost the same concluding argument can be made for Figure 2-8 as for Figure 1-8. Just like for Figure 1-8, this is a conceptual universal diagram, now for nanoassembly. It can cover a wide range of different nanoassemblies with a wide range of sizes and types of building units. Once the reference point (the point of initial force balance) is determined, this diagram provides the general tendency of the nanoassembly process and its outcome in a controlled manner with a reasonable prediction power. It works like a typical phase diagram and can be used in parallel with Figure 1-8. One difference is that, for Figure 1-8, there will not be any self-assembly that occurs outside the boundary while inside of it will always be a region where self-assembly occurs. For Figure 2-8, however, there can be a nanoassembly even at the region outside the boundary of the diagram. For example, outside the boundary of the right-hand side of the diagram in Figure 1-8, self-assembly system will be precipitated out rather than self-assemble. For nanoassembly system, on the other hand, this off-the-diagram region could promote an even more effective nanoassembly process with very high yield. Detailed use of Figure 2-8 is the same as Figure 1-8. We can simply follow the grid from the reference point to the point of interest or just jump to that point of interest. The nanoassembly systems at the points in between these two points (of reference and of interest) will almost always have the nanoassembly tendency in between those at the two points. There is also a good possibility that the nature of their nanoelements is in between those at the two points.

2.6. SELF-ASSEMBLY, NANOASSEMBLY, AND NANOFABRICATION

This section clarifies the relationship among self-assembly, nanoassembly, and nanofabrication, which are the three main assembly routes for nanotechnology systems. Different literature often uses these terms in quite different ways, which

TABLE 2-3. Definition of self-assembly (SA), nanoassembly (NA), and nanofabrication (NF); of self-assembled aggregate (SAA), nanoassembled system (NA-S), nanofabricated system, and nanointegrated system; and of nanodevice and nanomachine. SA-BU and NA-BU refer to self-assembly and nanoassembly building units, respectively.

SA	thermodynamic or kinetic assembly of **SA-BU**s
NA	thermodynamic, kinetic, or manipulative assembly of **NA-BU**s
NF	thermodynamic, kinetic, manipulative, or mechanical assembly of **NA-BU**s and bulk materials
SAA	aggregates formed via **SA**
NA-S	aggregates or systems assembled via **NA**
nanofabricated system	functional systems fabricated via **NF**
nanointegrated system	functional system integrated with or more nanofabricated systems via **NF**
nanodevice	nanofabricated systems that have unit operation capability
nanomachine	nanointegrated systems that have communication capability with macroworld

implies that there is a lack of general consensus. The relationship that is described in this section is not a definite one. But it provides a good understanding for the structure and hierarchy of different assembly routes when designing nanotechnology systems.

Table 2-3 shows the definition of self-assembly, nanoassembly, and nanofabrication. It also shows the definition of self-assembled aggregate and nanoassembled system. The last two rows are for the definition of nanofabricated and nanointegrated systems, and of nanodevice and nanomachine. Self-assembly is a thermodynamic or kinetic assembly of self-assembly building units. Nanoassembly is a thermodynamic, kinetic, or manipulative assembly of nanoassembly building units. Manipulative assembly here means the assembly of nanoassembly building units achieved by a one-by-one type of manipulation, for example, by using atomic force microscopy. Nanofabrication is a thermodynamic, kinetic, manipulative, or mechanical assembly of nanoassembly building units often with bulk materials. Thereby, nanoassembly includes self-assembly and nanofabrication includes nanoassembly. Self-assembled aggregate is an aggregate formed through self-assembly. A nanoassembled system is an aggregate or system assembled through nanoassembly. This means that a nanoassembled system includes all self-assembled aggregates, but not all self-assembled aggregates are nanoassembled systems.

A nanofabricated system is a functional system fabricated through nanofabrication. It thus includes all self-assembled and nanoassembled aggregates and systems. It also includes a nanoscale system or nanosystem fabricated with the aid of top-down methods. A nanointegrated system is a functional system where two or more nanofabricated systems are integrated into a single system through nanofabrication. A nanodevice is a nanofabricated system that has the capability of unit operation while a nanomachine is a nanointegrated system that has the capability of communication with the macroworld. A critical difference is that a nanodevice and a nanomachine have specific operational types of applications. They can become a

part of a macrodevice or macromachine that is at the stage of development or a part of existing devices such as a spectrometer and end-user products. For example, a nanoelectronic device (or nanoscale electronic device) is a macroscopic device that contains a nanoassembled system, nanofabricated system, or nanointegrated system as a part of its functional components. But an electronic nanodevice is a device that is composed of a nanodevice with a proper nanoelement (in this case, electronic property nanoelement) and whose size is mainly within the nanoscale. Therefore, nanoϕϕϕ machine (or nanoscale ϕϕϕ machine) is a macroscopic machine that contains a nanoassembled system, nanofabricated system, or nanointegrated system as a part of its mechanical functions (ϕϕϕ here represents any type of practical words such as *electronic*, *magnetic*, *optical*, etc.). But ϕϕϕ nanomachine is a machine that is composed of a nanomachine with a proper nanoelement (in this case, mechanical or communication nanoelement) and whose size is mainly within the nanoscale.

The diagram in Figure 2-9 summarizes the relationship and hierarchy between self-assembly, nanoassembly, and nanofabrication, and their assembled aggregates and systems. Some nanoassembly is purely self-assembly. Likewise, some nanofabrication is nanoassembly where no significant top-down processing is involved during the assembly process. Both nanofabricated system and nanointegrated system are the results of nanofabrication; thus they include nanoassembled system. And nanoassembled system includes self-assembled aggregate. Some nanoassembled systems are purely self-assembled aggregates. Likewise, many nanofabricated

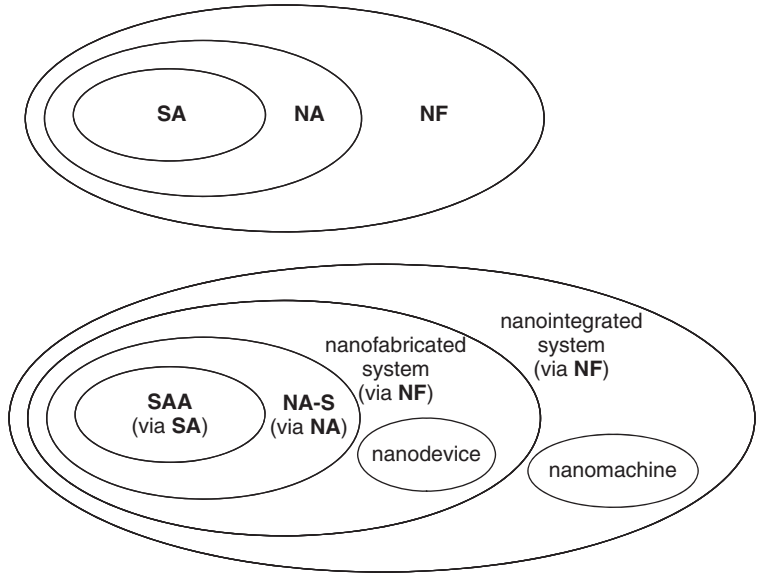


Figure 2-9. Relationship and hierarchy between self-assembly (**SA**), nanoassembly (**NA**), and nanofabrication (**NF**); between self-assembled aggregate (**SAA**), nanoassembled system (**NA-S**), nanofabricated system, and nanointegrated system; and between them and nanodevice and nanomachine.

systems and nanointegrated systems are nanoassembled systems. The term *nanotechnology system* that was introduced at the beginning of this chapter is the broadest one, which is meant to embrace all of these assembled, fabricated, and integrated aggregates and systems.

2.7. COLLECTION OF BUILDING UNITS

This section has the collection of nanoassembly building units. All of them are collected along with the self-assembly building units that are shown in Section 1.5. Thus, they are those published upto 2010. Because of their huge diversity, especially for fabrication building units, it is virtually impossible to cover them all in a single section. Shown in the tables are those that appear frequently across the different types of journals. For most of them, the routes for the preparation of each fabrication building unit are now well established and characterized. And the related details are also well published. This includes ligand substitution, ligand dynamics and orientation, and hydration/solvation states. Their assembly into nanotechnology systems is now widely exercised in many different fields.

The collection in this section is divided into five different groups and presented in six separate tables. The first two groups are two typical types of fabrication building units: ligand-protected nanoparticles and functional surfaces. Reactive building units are in the third group, and common substrates are shown as another separate group. Reducing agents are those that are used for the preparation of nanoparticles and ligand-protected nanoparticles (mainly metals). They are not exactly a family of nanoassembly building units, but play an important role in that regard. The most common ones are summarized in one table. As will be stated in the following subsections, each group of nanoassembly building units has a similar combination of segmental structure. Because of their own diversity and the diversity of environmental conditions where actual nanoassembly takes place, this may be played out somewhat differently. However, the pattern of nanoassembly within the same group is very similar in general and the outcome of their nanoassembly, that is, nanoelements, can be followed with a similar general tendency. This in turn provides a good foundation for the development of practical fabrication routes for a variety of nanotechnology systems and their applications.

2.7.1. Ligand-Protected Nanoparticles

Tables 2-4 and 2-5 have the collection of the most typical types of fabrication building units: ligand-protected nanoparticles. Table 2-4 is for the metal nanoparticles and Table 2-5 is for the non-metal nanoparticles. As the general scheme in Table 2-4 shows, this fabrication building unit refers to each nanoparticle with proper ligand molecules covered on its surface. For both tables, the nanoparticles and ligands are listed in separate columns. This is to show that there is not much specific selectivity between the nanoparticles and ligands. Except for the rare cases where the

TABLE 2-4. Collection of the nanoassembly building units that can be classified as a fabrication building unit: ligand-protected metal nanoparticles (nanoclusters) and their general scheme.[1] A, R, and D[c] refer to attractive, repulsive, and conditional directional segments, respectively; n is an alkyl chain, and the most common ones are shown for each homologue series.

Nanoparticle[a]	Ligand	Segment Combination[b]
gold	n-alkanethiol (n = hexyl−octadecyl)	**A**+**R**
silver	n-alkylmercury acetate (n = octyl−hexadecyl)[e]	**A**+**R**
platinum	n-alkylmercury chloride (n = octyl−hexadecyl)[e]	**A**+**R**
palladium	α,ω-alkanedithiol (n = hexyl−octadecyl)	**A**+**R**+**D**[c]
rhodium	ω-mercapto alkanol (n = hexyl−octadecyl)	**A**+**R**
mercury[d]	ω-mercapto alkanoic acid (n = hexyl−octadecyl)	**A**+**R**
	ω-mercaptoalkanetrimethoxysilane (n = hexyl−octadecyl)	**A**+**R**+**D**[c]
	benzenethiol	**A**+**R**
	triphenylphosphine	**A**+**R**
	trioctylphosphine	**A**+**R**
	n-alkaneselenol (n = octyl−tetradecyl)	**A**+**R**
	benzeneselenol	**A**+**R**
	diphenyl diselenide	**A**+**R**
	dialkyl disulfide (n = butyl−tetradecyl)	**A**+**R**
	dialkyl diselenide (n = butyl−tetradecyl)	**A**+**R**
	dialkyl ditelluride (n = butyl−tetradecyl)	**A**+**R**

[1] For more about the synthesis and characterization of ligand-protected metal nanoparticles, please see Nath et al., 2010.

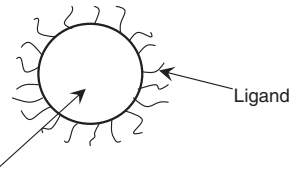
[a] Shown are representative ones. Most of the metal, bimetal, and alloy nanoparticles in Table 1-4 are also included.

[b] of fabrication building units, not of nanoparticles or ligands themselves.

[d] When the temperature is low enough. At room temperature, thiols form self-assembled monolayer on its surface.

[e] Usually shows improved resistance against aerial oxidative degradation than thiol-based ligands.

General scheme:



experimental conditions are very specific, any nanoparticles can be matched with any ligands to form a fabrication building unit. Segment combinations are shown in the third column. They are those of fabrication building units, not of nanoparticles or ligands themselves. More specifically, they represent the segment combination of the ligand-protected nanoparticle in which each ligand in the second column covers any of the nanoparticles in the first column. For most of them, the segment combination is very similar. They have the combination of attractive and repulsive segments while some of them have a conditional directional segment. This conditional directional segment has the same definition and function as in Subsection 1.5.2, which was for self-assembly building units. Figures 7-2(b), 8-3(c), and 14-4(d) have the full description for the segmental analysis of the ligand-protected

TABLE 2-5. Collection of the nanoassembly building units that can be classified as a fabrication building unit: ligand-protected nanoparticles (non-metals, metal oxides, and polymeric). The general scheme is the same as in Table 2.4. A, R, and D[c] refer to attractive, repulsive, and conditional directional segments, respectively; n is an alkyl chain, and the most common ones are shown for each homologue series.

Nanoparticle[a]	Ligand	Segment Combination[b]
silicon	3-aminopropyltrimethoxysilane	**A**+**R**
silica	3-aminopropyltriethoxysilane	**A**+**R**
tungsten oxide	3-aminopropyltrichlorosilane	**A**+**R**
iron oxide	dichlorodimethylsilane	**A**+**R**
mica	methyltrichlorosilane	**A**+**R**
alumina	alkanoic acid, ω-(triethoxysilyl)- (n = hexyl−octadecyl)	**A**+**R**
quartz	n-alkyltriethoxysilane (n = hexyl−eicosyl)	**A**+**R**
carbon nanotube	n-alkyltrimethoxysilane (n = hexyl−eicosyl)	**A**+**R**
fullerene	n-alkyltrichlorosilane (n = hexyl−eicosyl)	**A**+**R**
graphene	n-alkyldiethoxychlorosilane (n = hexyl−eicosyl)	**A**+**R**
	n-alkyldimethoxychlorosilane (n = hexyl−eicosyl)	**A**+**R**
	ω-mercaptoalkanetrimethoxysilane (n = hexyl−octadecyl)	**A**+**R**+**D**[c]
	(perfluoro-1,1,2,2-tetrahydroalkyl)trichlorosilane (n = octyl−octadecyl)	**A**+**R**
	n-alkylphosphonic acid (n = octyl−octadecyl)	**A**+**R**
polystyrene	poly(12-hydroxystearic acid)	**A**+**R**
poly(methyl methacrylic acid)		

[a]Shown are representative ones. Most of the nanoparticles in Table 1-4 other than metal, bimetal, and alloy ones are also included.
[b]of fabrication building units, not of nanoparticles or ligands themselves.

nanoparticles. Figure 14-4(j) has some special case of fabrication building unit that does not appear in the literature very often but that has an important implication for many nanotechnology systems. This fact that most of the ligand-protected nanoparticles, unless they are specifically modified to be otherwise, have very similar segment combination makes them follow very similar nanoassembly process. And the fact that the segment combination happens to be the most basic type makes the understanding of their nanoassembly quite practical, which otherwise could be very complicated and case dependent. Step-by-step discussions about this important point are shown in Figures 7-3(b), 7-4(a, c), 7-5(a), 8-5(a), and 8-6(a).

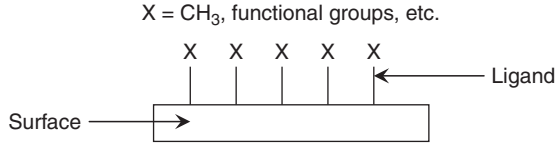
2.7.2. Functional Surfaces

Table 2-6 shows the collection of another type of fabrication building unit: functional surfaces. Like many ligand-protected nanoparticles, most of them have the basic type of segment combination. For some cases, the repulsive segment is conditional, which has the same definition and function as those for the self-assembly building units in Subsection 1.5.1. This similarity in segment combination between the two very different types of fabrication building units makes their nanoassembly

TABLE 2-6. Collection of the nanoassembly building units that can be classified as a fabrication building unit: functional surfaces and their general scheme. A, R, and R[c] refer to attractive, repulsive, and conditional (or negligible) repulsive segments, respectively.

Surface	Ligand	Segment Combination[a]
All of the nanoparticle elements in Tables 2-4 and 2-5 as surface[b]	All of the corresponding ligands in Tables 2-4 and 2-5[b]	The same as those corresponding in Tables 2-4 and 2-5
silicon substrate with oxidized surface layer		**A**+**R**
hydrogen-terminated silicon substrate		**A**+**R**[c]
metal, semiconductor, and alloy nanoislands nanopatterned on solid surfaces		**A**+**R**[c]
solid surfaces with polymer chains grafted		**A**+**R**

[a]of fabrication building units, not of surfaces or ligands themselves.
[b]This is a typical condition for the formation of self-assembled monolayer (SAM). For more about the preparation, property, and characterization of self-assembled monolayer of thiols, please see Love et al., 2005.
General scheme:



very comparable to each other. Chapters 7 and 8 cover the assembly principles between different types of nanoassembly building units, emphasizing the benefit of this fact. Chapters 11, 12, and 13 present the assembly principles for nanostructures, nanoproperties, and nanofabricated systems, respectively, also benefiting from this fact.

2.7.3. Reactive Precursors

Table 2-7 is the collection of reactive building units. Figure 2-4 showed three different types of reactive building units. But shown in this table are those with only a reactive part. This is not to ignore the other two types but to emphasize that, with a few exceptions, the reactive building units with a reactive part only are the most abundant ones and also easy to work with during nanoassembly, because of their simple segmental structure. All of those shown have only an attractive segment. Full descriptions of the segmental structure of each reactive building unit are presented in Figures 7-2(c), 8-3(d), 11-2(e), 12-2(e), and 13-2(c).

2.7.4. Substrates

For many nanoassembly systems, substrates play an important role either by providing a crucial directionality or assemblity to the nanoassembled systems or even

TABLE 2-7. Collection of the nanoassembly building units that are a reactive building unit. A refers to attractive segment.

Name	Segment Combination
silicate anion	**A**
tetramethyl orthosilicate	**A**
tetraethyl orthosilicate	**A**
methyltrimethoxysilane	**A**
1,2-bis(triethoxysilyl) ethane	**A**
titanium tetrachloride	**A**
titanium tetraisopropoxide	**A**
titanium trichloride	**A**
tetrabutyl orthotitanate	**A**
tetrachloroauric acid	**A**
tetrachloroplatinic acid	**A**
2,2-dimethyl propanoic acid, zirconium(4+) salt	**A**
metal vapor e.g., gold, silver, germanium, indium	**A**
semiconductor vapor	**A**

by becoming a part of the nanoassembled systems. However, for many other nanoassembly systems, substrates are just substrates. They do not provide any meaningful directionality or assemblity to the nanoassembled systems. They merely act as a supporter and the different nature of substrates hardly brings any different outcomes. This different perspective on the substrates is solely dependent on the nature of each nanoassembly system. Table 2-8 is the collection of the most commonly used substrates. Their segment combinations are usually basic: attractive segment combined with conditional repulsive segment. But depending on their structures, such as pore or channel, they often have conditional directional segment as well. This is the main reason that most of the substrates can be viewed as another self-assembly building unit during any assembly processes, which brings a much more simplistic way to understand the substrate-involved assembly and fabrication and to establish general trends out of the outcomes. This issue will be explained in Figures 11-2(c), 12-2(d), 13-2(b), and 14-4(f). The definition and function of the conditional repulsive and conditional directional segments are the same as those in Subsections 1.5.1 and 1.5.2, respectively.

2.7.5. Reducing Agents

Table 2-9 is the collection of the reducing agents that are commonly used for the synthesis of metallic nanoparticles. They rarely become a part of the nanoassembled systems. However, the reducing agents often play a significant role in the structural control of the nanoassembled systems.

2.8. CONCLUDING REMARKS

This chapter showed the concept of the three basic nanoassembly building units for the development of nanotechnology systems. It also showed that the assembly

TABLE 2-8. Collection of the substrates that are commonly used for self-assembly, nanoassembly, and nanofabrication. A, R, R^c, and D^c refer to attractive, repulsive, conditional (or negligible) repulsive, and conditional directional segments, respectively.

Substrate	Segment Combination
silicon	**A**+$\mathbf{R}^c$
silica	**A**+$\mathbf{R}^c$
quartz	**A**+$\mathbf{R}^c$
highly oriented pyrolytic graphite (HOPG)	**A**+$\mathbf{R}^c$
diamond (bare, hydrogen-terminated)	**A**+$\mathbf{R}^c$
diamond-like carbon (DLC)	**A**+$\mathbf{R}^c$
indium tin oxide (ITO)	**A**+$\mathbf{R}^c$
metals	**A**+$\mathbf{R}^c$
e.g., gold, silver, copper, aluminum, platinum	
glass slide, borosilicate glass	**A**+$\mathbf{R}^c$
gallium arsenide	**A**+$\mathbf{R}^c$
zinc selenide	**A**+$\mathbf{R}^c$
calcium carbonate	**A**+$\mathbf{R}^c$
calcite	**A**+$\mathbf{R}^c$
sodium chloride	**A**+$\mathbf{R}^c$
YSZ (yttrium zirconium oxide)	**A**+$\mathbf{R}^c$
silicon carbide	**A**+$\mathbf{R}^c$
zirconium carbide	**A**+$\mathbf{R}^c$
316L stainless steel	**A**+$\mathbf{R}^c$
AISI 52100 (iron-based alloy)	**A**+$\mathbf{R}^c$
silicon nanogroove	**A**+$\mathbf{R}^c$+$\mathbf{D}^c$
silica nanopore	**A**+$\mathbf{R}^c$+$\mathbf{D}^c$
nanochannel: glass, anodic alumina membrane	**A**+$\mathbf{R}^c$+$\mathbf{D}^c$
montmorillonite, layered	**A**+$\mathbf{R}^c$+$\mathbf{D}^c$
kaolinite	**A**+$\mathbf{R}^c$+$\mathbf{D}^c$
bentonite	**A**+$\mathbf{R}^c$+$\mathbf{D}^c$
saponite	**A**+$\mathbf{R}^c$+$\mathbf{D}^c$
sepiolite	**A**+$\mathbf{R}^c$+$\mathbf{D}^c$
All functional surfaces in Table 2-6	The same as in Table 2-6

principles for nanotechnology systems are fundamentally the same as for self-assembly systems. Just as we assemble the self-assembled systems through the logical combination of the five segments, nanotechnology systems can be obtained through the logical combination of the three basic nanoassembly building units. In addition to that, the main working forces and their working distances are almost identical for self-assembly and nanoassembly systems. The same concept of force balance can be applied for both assemblies to explain and to design their assembly processes and for the formation of their assembled aggregates and systems.

Imagine the LEGO toys from the beginning of this chapter. We know that almost limitless possibilities can be explored by simply combining those basic parts through simple logic yet with playful thinking. And more functions can be added onto the action figures by exploring the possibilities of creating new parts that did not exist in the first place and through the logical combination of the basic parts. Building nanotechnology systems can be explored just like building these functional LEGO toys. There are endless possibilities in nanoassembly building units that can be tested and there are endless possibilities of combinations that can be imagined between them. As long as the force balance is satisfied between the

TABLE 2-9. Collection of the reducing agents that are commonly used for the synthesis of metallic nanoparticles.

Chemical Name
citric acid
L-ascorbic acid
L-tryptophan
certain peptides
sodium borohydrate
lithium triethylborohydride (superhydride)
9-borabicyclo[3.3.1] nonane
poly(*o*-methoxy aniline)
hydroquinone

building units, they should be able to assemble one way or another and should show at least one of the four nanoelements.

Finally, it is worth emphasizing how and why self-assembly and nanotechnology systems are so inseparable. It is not just because they are governed by the same type of working forces. More importantly, they complement each other. Self-assembly systems provide a powerful means for nanotechnology systems, from assembly all the way to device operations. Furthermore, the issues of nanotechnology inspire us with a great magnitude so that they encourage us to develop a constant flow of new self-assembly building units and self-assembled aggregates. As nanotechnology is quickly and broadly moving forward, these important aspects will bring more fruitful outcomes to us. Realization of great artificial systems based on the fusion of nanotechnology, biotechnology, informatics, and cognitive science (Amato, 2005; Bainbridge, 2007; Ho et al., 2006) will be one step closer with this.

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Part II

Design

3

Identification of Self-Assembly Capability

3.1. ASSEMBLY ISSUE

This first chapter of the second part begins with the fundamental question that covers the entire spectrum of self-assembly systems. The question to be addressed here is:

> *Will a given potential self-assembly building unit actually self-assemble in a given experimental condition?*

And the question goes one step further:

> *If so, how can it be determined?*

The definition of self-assembly was presented in Chapter 1. As will be shown throughout this chapter, this first fundamental question about self-assembly can be well addressed in a qualitative way and, in many cases, a semiquantitative way, by carefully analyzing the structures of self-assembly building units via *segmental analysis* (Subsection 1.2.2). It will be shown that the prediction of the self-assembly capability of a given potential building unit can be achieved in a surprisingly systematic manner once its segmental structure has been properly analyzed. This will continue in subsequent issues regarding self-assembly systems in the following chapters. The capability of self-assembly building units for higher orders of self-assembly processes will be addressed in Chapter 4. The structural determination

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of the self-assembled aggregates formed at each step of the self-assembly process will be presented in Chapter 5. And questions about the hierarchy and chirality that are especially important for the applications of self-assembly systems will be discussed in Chapter 6.

3.2. GENERAL OVERVIEW

Figure 3-1 shows a general overview of the identification of the self-assembly capability of a given self-assembly building unit. It is based on segmental analysis (see Subsection 1.2.2 for details). Let us assume that there is an atom, molecule, polymer, or colloidal particle regarding which we want to find out whether it can self-assemble. Let us call it a *potential* self-assembly building unit. The first step to achieve this goal is getting the structural picture of the building unit as precisely as possible. Its segmental analysis should then be pursued. This step is purely empirical. No experiment or simulation is involved. Details for this analysis are presented in the next section. Once all segments of the potential self-assembly

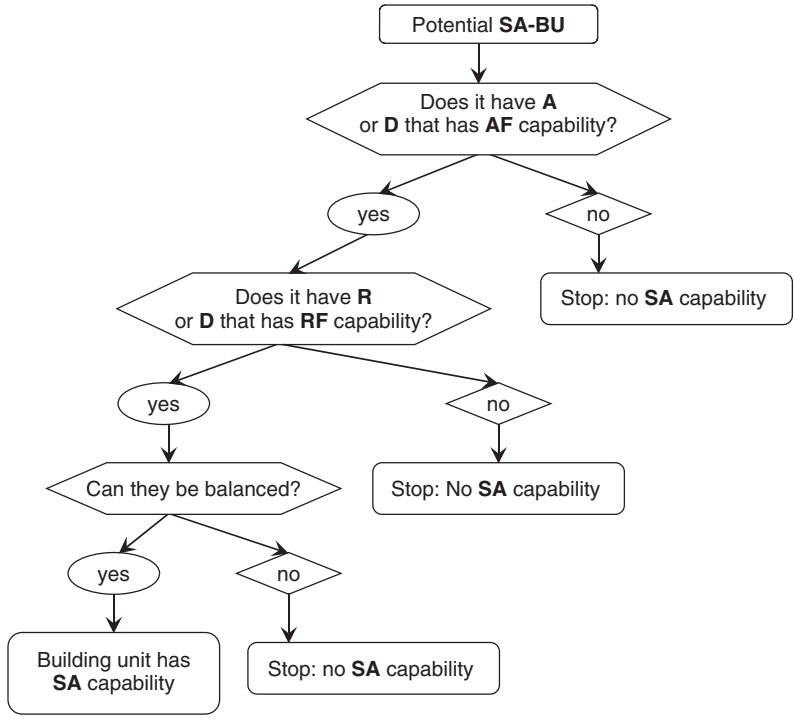


Figure 3-1. General overview for the identification of the self-assembly capability of a given self-assembly building unit (**SA-BU**). **SA** is short for self-assembly. **A, R**, and **D** refer to attractive, repulsive, and directional segments, respectively. **AF** and **RF** refer to attractive and repulsive forces, respectively.

building unit have been identified and assigned, the first observation that should be made is whether this potential building unit has an attractive segment or a directional segment that has a capability of an attractive force. To be able to self-assemble for this building unit, this attractive force should be strong enough to bring the building units closely together. If the answer is no for this first question, then it will be safe to conclude that this building unit does not have the capability of self-assembly. In other words, it cannot be an effective self-assembly building unit unless a strong enough external force is imposed to force it to assemble. (This issue will be discussed in Chapter 8.) On the other hand, if the answer is yes, then we can go on to the next step and ask whether this building unit has a repulsive segment or a directional segment that has the capability of a repulsive force. If the answer is no for this second question, then this building unit cannot be called a self-assembly building unit. It might have a strong possibility to keep aggregating until it is precipitated out if it is in solutions, or of forming a bulk material if it is in contact with surfaces. However, if the answer is yes, the critical observation to be made is whether these two different types of forces (an attractive force and a repulsive force) can be balanced. If the answer is no for this third question, then again this building unit cannot become an effective self-assembly building unit. It will either keep aggregating if the attractive force is dominant, or simply be dissipated out if the repulsive force is dominant. However, if the answer is yes, then it can be concluded that this building unit will self-assemble, thus becoming an effective self-assembly building unit.

One critical question while following this flowchart is how the balancing of the attractive force with the repulsive force can be determined. This is where the reference self-assembly system (Figure 1-6) comes into play. This will be described in the next section with examples.

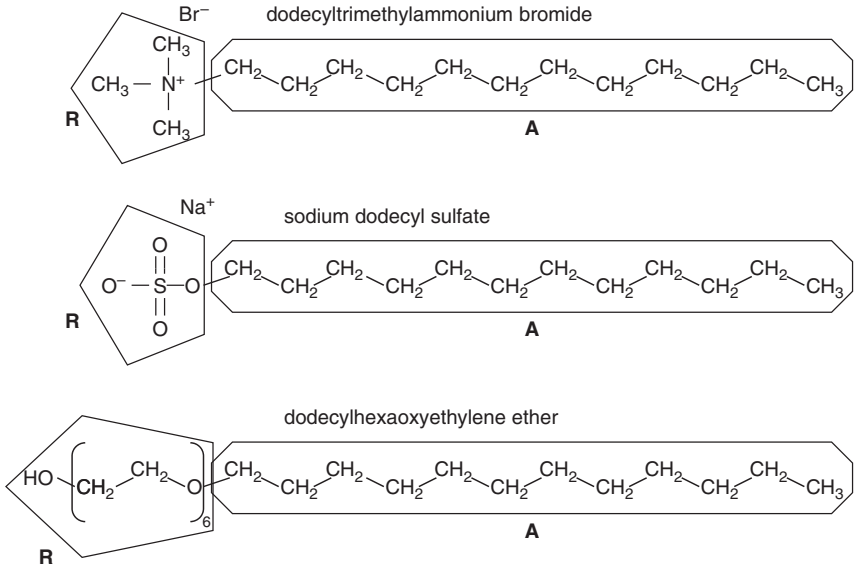
3.3. ASSEMBLY PRINCIPLES

Some representative self-assembly systems will be analyzed based on segmental analysis and the flowchart from the previous section. Of course, there are many other self-assembly systems other than those that are presented in this section. However, once the concept of segmental analysis is established for these representative cases, its expansion to similar systems will be much easier. For instance, no atomic or polymeric self-assembly systems are presented in this section. But the analysis for the determination of their self-assembly capability is fundamentally the same as for the molecular and colloidal self-assembly systems. Some self-assembly systems that take place on surfaces are presented in the final subsection.

3.3.1. Molecular Self-Assembly

Figures 3-2, 3-3, and 3-4 have schematic explanations of the self-assembly of different surfactant molecules. They show how their self-assembly capability can be determined through segmental analysis of their molecular structures. They also

(a) **SA-BU**s



(b) Schematic illustration

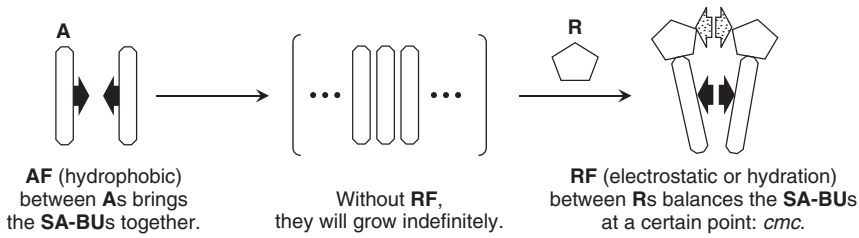

A
R
AF (hydrophobic) between As brings the SA-BUs together.
Without RF, they will grow indefinitely.
RF (electrostatic or hydration) between Rs balances the SA-BUs at a certain point: cmc.

Figure 3-2. Schematic explanation for the self-assembly of surfactant molecules that have the combination of attractive (**A**) and repulsive (**R**) segments. **SA-BU** is short for self-assembly building unit. **AF** and **RF** refer to attractive and repulsive forces, respectively. *cmc* is critical micellar concentration.

show how the general tendency of their self-assembly capability can be determined for their homologous series.

Figure 3-2(a) shows three different surfactant molecules. Dodecyltrimethylammonium bromide is a typical cationic surfactant. The name *cationic* comes from the fact that its head group possesses a positively charged atom. Sodium dodecyl sulfate and dodecylhexaoxyethylene ether are typical anionic and nonionic surfactants, respectively. Again the names *anionic* and *nonionic* come from the molecular characteristics where the former has a negatively charged atom in its head group and the latter has no charges in its head group. All three surfactant molecules have the same dodecyl chain. A hydrocarbon chain of twelve-carbon is one of the typical

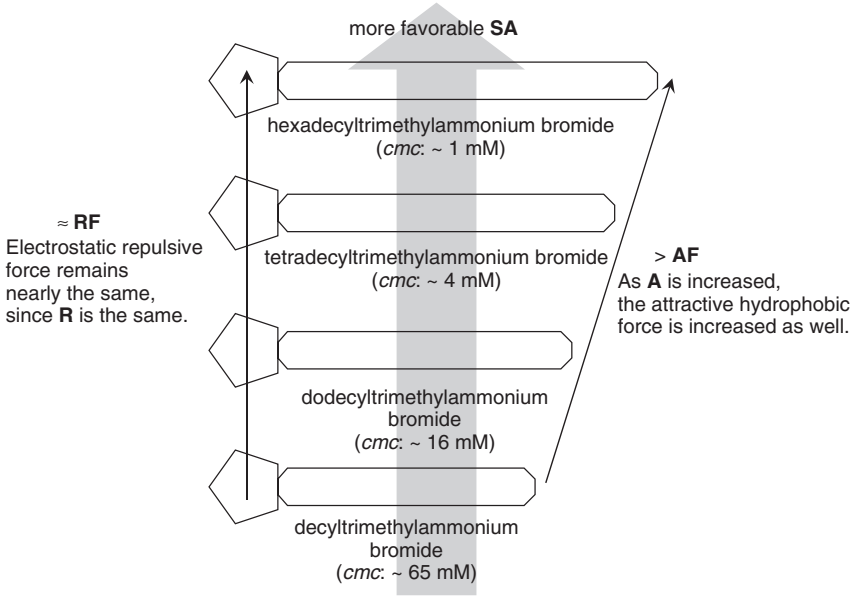


Figure 3-3. Self-Assembly of typical ionic surfactants: alkyl trimethyl ammonium bromides. **SA** is short for self-assembly. **A** and **R** refer to attractive and repulsive segments, respectively. **AF** and **RF** refer to attractive and repulsive forces, respectively. *cmc* is critical micellar concentration.

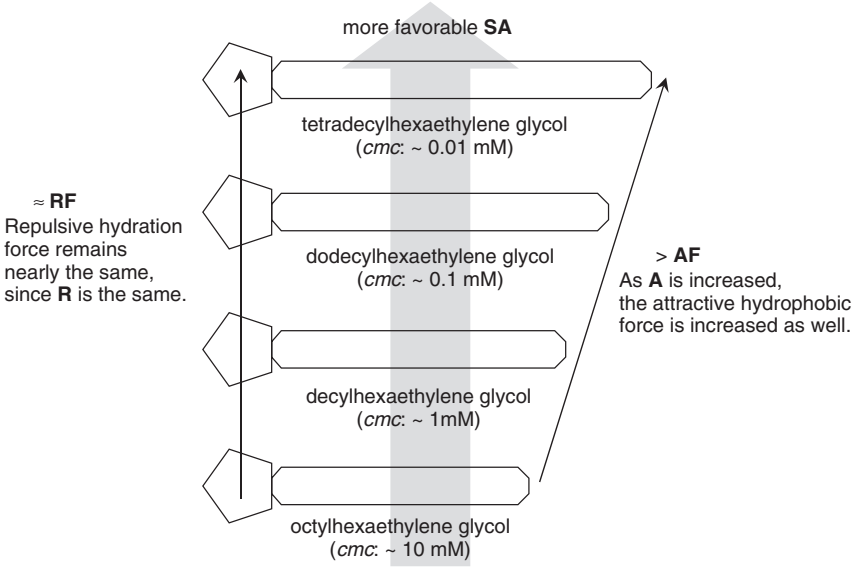


Figure 3-4. Self-Assembly of typical nonionic surfactants: alkyl hexaethylene glycols. **SA** is short for self-assembly. **A** and **R** refer to attractive and repulsive segments, respectively. **AF** and **RF** refer to attractive and repulsive forces, respectively. *cmc* is critical micellar concentration.

attractive segments for self-assembly building units because it can easily attract nearby self-assembly building units through its hydrophobic interaction. Thus, the dodecyl chain for all three can be designated as an attractive segment. The symbol of an elongated octagon is used to represent this attractive segment (details in Figure 1-3). All three molecules, on the other hand, have different natures of head groups. But once each of the molecules gets close enough through the attractive force induced by the attractive segment, all of these head groups act as a repulsive segment for the self-assembly. Cationic head groups will repel each other through the electrostatic repulsive force, and anionic head groups will do the same. Nonionic head groups will repel each other through the repulsive hydration force. The symbol of a pentagon is used to represent this repulsive segment (details in Figure 1-3). Thus, this is a case of a molecular self-assembly building unit that consists of only two fundamental segments: attractive and repulsive ones. This is one of the most abundant types of self-assembly building unit (for a list of them, refer to Table 1-4), thus it makes a good starting point from which to go further into more complicated self-assembly systems.

Figure 3-2(b) shows the schematic illustration. This is not actually what happens in a self-assembly system under any conditions. This is to guide the analysis of the self-assembly process. As stated in the previous section, always consider the attractive segment first. In this case, the attractive segment is the hydrocarbon chain that generates hydrophobic attractive force. When the hydrocarbon chains happen to be close enough, mostly by diffusion, to be able to interact through this hydrophobic attractive force, they will bring the self-assembly building units together. For the next step of analysis, if we consider the situation where there is no segment within the self-assembly building unit that can counterbalance this attractive process, they will just keep growing indefinitely until all of them are exhausted from the source. This is not a self-assembly. All three surfactant molecules in Figure 3-2(a) have a repulsive segment. When they are close enough, these repulsive segments come into play, which means that they counterbalance the attractive force. It will be either through an electrostatic repulsive force (for cationic and anionic surfactants) or through a hydration force (for nonionic surfactant). As this process is preceded, the repulsive force will eventually reach the point where it is apparently balanced with the attractive force. Other dynamic processes during self-assembly including counterion binding/releasing, monomer exchange, and breakup/reassembly of the whole self-assembled aggregates (micelles) will certainly continue to happen. However, the apparent assembly process will be equilibrated at this point of force balance. This is a self-assembly process of this type of self-assembly building unit. The point where the two opposite forces are balanced can be expressed with self-assembly parameters. One of the prominent ones is *cmc* (critical micellar concentration).

This simple analysis is not necessarily limited to molecular self-assembly building units from this figure. Many other surfactant molecules with more complex segmental structures and many amphiphilic polymers can be subjected to the same analysis for their self-assembly. The same analysis is also applied to the self-assembly of colloidal particles and even bigger objects regardless of their geometrical differences. As long as they belong to the same type of segmental

structure (one attractive segment combined with one repulsive segment), the principle of their self-assembly is the same. It will be constructive to refer to the recent computational study that shows that the self-assembly process of a biologically derived amphiphile follows a very similar scenario to the one described here (Yan et al., 2007). So is the Monte Carlo simulation report (Bianchi et al., 2007) for the description of an equilibrium self-assembly process whose key is to adopt the concept that the attractive interaction for the self-assembly is localized in a specific part of the particle surface (patchy interaction).

3.3.1.1. Ionic Surfactants. Figure 3-3 shows the self-assembly of a typical homologue series of cationic surfactants: alkyltrimethylammonium bromides. Four of them are shown in the figure, but the general tendency of their self-assembly that will be drawn in this subsection certainly covers other members of this series as well. For the sake of simplicity, actual molecular structures are not included. Only the symbols that represent each segment are shown.

The four surfactant molecules shown are decyl-, dodecyl-, tetradecyl-, and hexadecyltrimethylammonium bromides. All of them have exactly the same repulsive segment, which is the trimethylammonium group. This is positively charged. The attractive segment for all four molecules is their hydrocarbon chains. The difference, however, lies in their length. From the bottom (decyl-) to the top (hexadecyl-), the hydrocarbon chain length is increased as an increment of two-carbon. This means that the size of the attractive segment is increased in a systematic way. Thus, it can be simply interpreted that, as we go from the bottom to the top molecule, the hydrophobic attractive force is also increased in a systematic way. It is assumed here that experimental conditions are the same for all four molecules. Meanwhile, the repulsive force, which is an electrostatic force, should remain nearly the same since the repulsive segments are exactly the same for all four molecules. This analysis leads us to conclude that, as we go from the bottom to the top molecule, the balance between the attractive and repulsive forces should occur earlier. There is simply more attractive force as we go to this direction. This means that the self-assembly should be more favorable as the hydrocarbon chain length is increased within this homologue series. This is certainly evidenced by *cmc* values. When the self-assembly is more favorable, in other words, when the force balance occurs earlier, *cmc* value should be decreased because the self-assembly should happen with smaller concentrations of self-assembly building units. At room temperature in aqueous solution, the *cmc* value of decyl-trimethylammonium bromide is $\sim$65 mM. For dodecyl-, it is decreased to $\sim$16 mM. And tetradecyl- and hexadecyl- have their *cmc* values of $\sim$4 mM and $\sim$1 mM, respectively. As expected, the *cmc* values are decreased systematically, and follow the $\frac{1}{4}$ rule (decrease of 4 times) as the hydrocarbon chain length is increased with an increment of two-carbon.

This example shows that segmental analysis can be a simple but useful tool in following self-assembly processes. A simple structural consideration followed by the force balance approach provides a reliable estimation for self-assembly parameters. It was *cmc* values that we used here. But certainly other parameters, including the degree of counterion binding, micelle dynamics, and the structural

features of self-assembled aggregates, can be followed with the same analysis. As will be shown in Chapter 8, this analysis can be applied to the changes in experimental conditions such as temperature, pressure, pH, and ionic strength as well. Additional analysis that will be necessary is the change in each segment induced by each experimental condition.

3.3.1.2. Nonionic Surfactants. There are a variety of different types of nonionic surfactants. Many of them are commercially available and under industrial usage. Among the typical ones are those based on the polyoxyethylene ether group. Figure 3-4 shows one homologue series of this anionic surfactant. Once again, only the symbols representing each segment are shown in the figure.

Four self-assembly building units are presented in the figure. They are octyl-, decyl-, dodecyl-, and tetradecyl-hexaethylene glycols. The hydrocarbon chain part is an attractive segment for their self-assembly. The same logic from Figure 3-3 should be applied to this assignment. The length of hydrocarbon chain is increased with an increment of two-carbon from octyl- to tetradecyl-. This should be interpreted as an increasing of the attractive hydrophobic force. A repulsive segment for these surfactants is the hexaethylene glycol part. Unlike cationic and anionic surfactants, this repulsive segment does not have the capability for an electrostatic force. But if we assume that these surfactants are in aqueous solution at room temperature, the hexaethylene glycol part will surely be hydrated, which will induce a hydration force. Hydration force is one of the typical repulsive intermolecular forces that play a critical role in self-assembly. It is generated not just in pure aqueous solution but in a variety of water-based mixed solvent systems as well. All four surfactants have the same length of this repulsive segment, which can lead us to conclude that the repulsive hydration force remains nearly the same regardless of the difference in the length of hydrocarbon chains. For self-assembly building units of this type, an attractive segment and a repulsive segment are sometimes coupled to each other at some degree. This means that there could be a counteractive effect on this repulsive hydration force by the attractive hydrophobic force. However, as most of the known results in the literature have confirmed, this effect is minimal for self-assembly building units with long hydrocarbon chains like those in the figure. This fact justifies the analysis that the hydration force among these surfactants is the same. The rest of the self-assembly analysis should be the same as for the previous ionic surfactants.

As we go from the bottom (octyl-) to the top (tetradecyl-), the attractive force is increased while the repulsive force remains nearly the same. Literature results show that octylhexaethylene glycol, under the conditions mentioned above, self-assembles with its *cmc* value of ~10 mM. This leads us to pick this particular one as a reference self-assembly system for this homologue series. As for decyl-, dodecyl- and tetradecylhexaethylene glycols, it is now inevitable to conclude that they also should self-assemble. And it should be more favorable. It is also obvious that this should be reflected by a gradual decreasing of their *cmc* values. Literature values show that this is indeed the case. Decyl- and dodecylhexaethylene glycols have ~1 mM and ~0.1 mM of *cmc*, respectively. And tetradecylhexaethylene glycol has ~0.01 mM of *cmc*. Notice that there is a clear difference between the ionic

surfactants (Figure 3-3) and the nonionic surfactants. For this nonionic surfactant series, the *cmc* values were decreased 1/10 in ratio as the length of the attractive segment (hydrocarbon chain) was increased as an increment of two-carbon. With exactly the same set of attractive segment conditions, the ionic surfactants showed the $\frac{1}{4}$ rule of *cmc* decrease. This difference can also be addressed with segmental analysis. Electrostatic repulsive force is a force that acts on a much wider range of distance than hydration force. Its absolute magnitude is greater than the one of hydration force when they are compared at the same distance. Thus, in most situations, the impact of electrostatic repulsive force is stronger than hydration force. Simply stated, there is more repulsive force for ionic surfactants (both cationic and anionic) than for this type of nonionic surfactant. But the hydrophobic force is the same hydrophobic force whether they are present in ionic surfactants or in nonionic surfactants. The result from this fact is that nonionic surfactants should experience steeper decreasing of *cmc* values than ionic surfactants as their hydrocarbon chain length is increased.

3.3.2. Colloidal Self-Assembly

As with the molecular self-assembly building units from the previous subsections, all of the colloidal self-assembly building units in this subsection are consist of two fundamental segments (one attractive segment and one repulsive segment). This is for the sake of having a consistent discussion.

Figure 3-5 shows a schematic explanation for the self-assembly of a colloidal self-assembly building unit. A silica nanoparticle with an arbitrary size but with a spherical shape is chosen as an example of colloidal particles. One important assumption is that its entire surface is covered with natural electric charges. At first glance, it may look quite different from a molecular self-assembly building unit. The structure of a silica nanoparticle itself does not seem to provide any clear-cut characteristics when designating which part is an attractive segment and which part becomes a repulsive segment. As will be seen throughout the book, this is quite common for colloidal self-assembly building units when it comes to performing a segmental analysis. However, if we focus on the core principle of the segmental analysis, which is the force balance between the building units, it comes easily to the point that colloidal particles are no different from molecular self-assembly building units. They may look different, but they still have the same fundamental segments for their self-assembly. Silica nanoparticles will always attract each other whenever they happen to be close enough. This is simply because there will be always a van der Waals attractive force between them. If the condition is properly set, there will be a depletion force as well, which is another typical attractive colloidal force. Thus, a silica nanoparticle itself should be identified as an attractive segment. As with molecular self-assembly building units, the symbol of an octagon is used to represent this. Its shape is modified to be a regular octagon just to fit into the spherical shape of the silica nanoparticle. Earlier we assumed that this silica nanoparticle has its natural surface electric charges on its entire surface. This assumption can be accepted as common practice since most nanoparticles (or

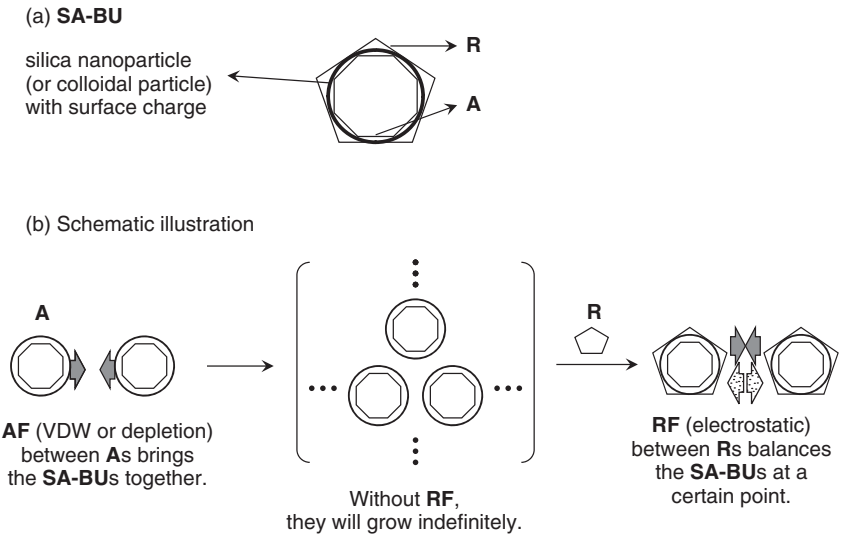


Figure 3-5. Schematic explanation for the self-assembly of colloidal particles that have the combination of attractive (**A**) and repulsive (**R**) segments. **SA-BU** is short for self-assembly building unit. **A** and **R** refer to attractive and repulsive segments, respectively. **AF** and **RF** refer to attractive and repulsive forces, respectively.

colloidal particles) have at least some degree of surface charges on their surfaces unless they are treated not to have them or to be neutralized. This helps us make the case for the repulsive segment of this silica nanoparticle. When they are close enough, these surface charges will act to repel each other. Thus, this surface charge should be identified as the repulsive segment of this silica nanoparticle. Again, the same symbol of a pentagon as for molecular self-assembly building units is used to represent this repulsive segment. To make the illustration clearer, both of the symbols of octagon and pentagon are drawn with a narrow line while the silica nanoparticle is represented with a bold line.

Figure 3-5(b) shows a schematic illustration of the proceeding of the self-assembly of this silica nanoparticle. As with the schematic illustration for molecular self-assembly building units shown in Figure 3-2(b), this is a schematic view to explain the process of the force balancing to achieve the self-assembly. This is not what is going to happen in an actual system. When the silica nanoparticles happen to be close enough, for example, through Brownian diffusion, the attractive segment acts to bring them closer through their van der Waals (or depletion) attractive force. Should there be no repulsive force within the silica nanoparticles, they will keep aggregating until all of the nanoparticles are depleted from the source. This silica nanoparticle, however, has a repulsive segment that can provide a repulsive electrostatic force. This force will act against the attractive force, and eventually the two opposite forces will be balanced at a certain point. This point is not a static one. Rather it is a dynamic point, just like the one for molecular

self-assembly building units. An individual silica nanoparticle still can come to join the aggregates and leave them within a very short time scale, but, in most cases, with a time scale slower than the one for molecular self-assembly building units. Whole aggregates can also break apart and reassemble instantly, also with a time scale slower than the one for molecular units. Their apparent size and weight are much larger and bigger than those of molecular aggregates. *cmc* was one of the practical self-assembly parameters that can be used to follow the molecular self-assembly processes. Traditionally, this is defined as the concentration of surfactant (or amphiphile) molecules at the point where the self-assembly begins to occur. For colloidal self-assembly building units, *can* (critical aggregation number) becomes a useful parameter for the same purpose. With the same sense of definition, it is the number concentration of colloidal particles at the point where the self-assembly begins to occur.

This picture of a colloidal self-assembly building unit is not necessarily limited to those with surface charges. Whenever there is an intrinsic (such as a geometrical) factor that can induce a repulsive force, the self-assembly process of other types of colloidal particles can be followed based on the picture shown here. Examples include nanoparticles (or colloidal particles) stabilized sterically in solutions and polymer particles that are intercoiled into a colloidal size. What is going to happen when the attractive segment and the repulsive segment have never been balanced is the same as for the silica nanoparticle with surface charges. If the repulsive segment does not provide enough balancing force, segmental analysis simply says that the colloidal particles will keep aggregating until all of them are precipitated out (in solutions, which is mostly the case). However, there could be no self-assembly at all if the repulsive force is simply too strong in overcoming the attractive force.

Case Study 3.1

The concept of *Janus balance* has recently been proposed in line with the effort to follow the self-assembly of Janus colloidal particles (particles whose surface have different chemical composition on two sides) (Jiang and Granick, 2007; 2008). It is based on the balance between the interaction from hydrophilic sides of a colloidal particle and the interaction from hydrophobic sides of a colloidal particle. This actually resembles the hydrophilic–lipophilic balance (HLB) of surfactant molecules for their emulsion formation. This article provides some helpful insight related to the above argument. So does the recent report that shows the effect of interparticle electrostatic repulsion for the agglomeration of semiconductor nanocrystals in aqueous solution (Zhang et al., 2008).

Case Study 3.2

There is another study that explains the role of the balance between the attraction and repulsion between charged soft colloidal particles in their self-assembly process and in the size and morphology of their self-assembled aggregates (Bordi et al., 2007). The work that reports the potential of mean force between two spherical like-charged macroions that covers the range from pure repulsive to

pure attractive potential of mean force is also worth reading in this regard (Reščič and Linse, 2008). A numerical work that draws a unifying theory for the self-assembly of colloidal particles through the competition between attractive and repulsive forces has led to predicting the range of a monomer–aggregate coexistence region and the dependence of the aggregation number on the colloid concentration (Destainville and Foret, 2008).

3.3.2.1. Colloids with Different Origins. Figure 3-6 shows four colloidal particles with different chemical natures. They are silica, polystyrene, bovine serum albumin, and gold particles. Each of them represents one of the typical colloidal particles from the groups of oxides, polymers, biological colloids, and metals, respectively. All the self-assemblies are considered under the same experimental condition, which is in water at room temperature. In addition, it is assumed that all of them have the same spherical shape with the same diameter.

The Hamaker constant is one critical parameter that can represent the strength and the direction of the van der Waals force. The Hamaker constant A of the four colloidal particles in the figure is 0.46, 0.911, 1.40–2.00, and 5.5–140, respectively in the given condition (Lee, 2008). The van der Waals force is the main contributing factor to the attractive segment for all four colloidal particles. The positive values of Hamaker constant indicate that they are attractive in this condition. And the increasing of its absolute value, from the left-hand side (silica) to the right-hand side (gold), means that this attractive van der Waals force is increased in this direction. In other words, the attractive force between the colloidal particles is increased in this direction. For a repulsive force, it is assumed that the density of the surface charge is the same for all four colloidal particles. This surface charge generates the repulsive electrostatic force, thus becoming the repulsive segment.

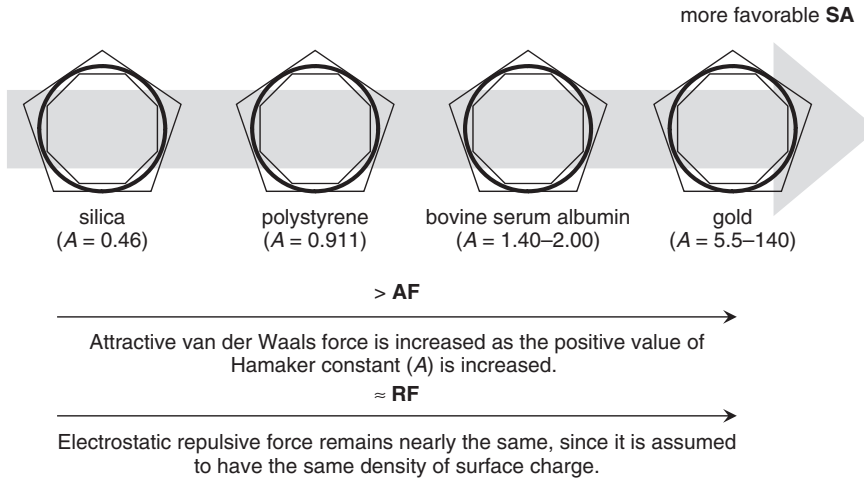

more favorable SA
silica
(A = 0.46)
polystyrene
(A = 0.911)
bovine serum albumin
(A = 1.40–2.00)
gold
(A = 5.5–140)
> AF
Attractive van der Waals force is increased as the positive value of Hamaker constant (A) is increased.
≈ RF
Electrostatic repulsive force remains nearly the same, since it is assumed to have the same density of surface charge.

Figure 3-6. Self-assembly of typical colloidal particles in water at room temperature. **SA** is short for self-assembly. **AF** and **RF** refer to attractive and repulsive forces, respectively.

This may not be a realistic assumption since the chemical nature of their surfaces is quite different. Also, the surface charge will be delicately dependent on the subtle change in experimental conditions. But let us remember that this assumption is to make the difference in self-assembly capabilities among different colloidal particles more understandable, even though it may not be always the case in real systems. With this in hand, now we have a very familiar setting of segmental structure. The attractive force is gradually increased as we go toward gold while the repulsive force remains nearly the same. Under the experimental condition that favors the self-assembly of silica particles, this segmental analysis tells us that the other three colloidal particles should also self-assemble under the same condition. And it should be more favorable self-assembly as we go toward gold. This should be, of course, reflected by the prominent changes in the self-assembly parameters for colloidal particles, including the decreasing of *can* and the increasing of the sizes of aggregates.

Notice that the Hamaker constant is with the unit of 10^{-20} J. Also, as stated in the previous subsection, this general tendency of self-assembly capability for colloidal particles is not limited to the colloidal particles with surface charges. It is not limited to the colloidal particles presented in this figure, either. Regardless of their physical characteristics, as long as a clear segmental analysis is performed, and as long as a reasonable reference system is indentified, this exercise can stand valid for many different types of colloidal particles as well.

Case Study 3.3

For an actual calculation work on the self-assembly of monodisperse semiconducting nanoparticles based on the notion of force balance, see Talapin et al. (2007). In terms of segmental analysis, van der Waals interaction and electrostatic force between the nanoparticles on their works are the attractive and repulsive segments, respectively. The same article also calculates the interaction of the nanoparticles with substrates. This is a surface self-assembly of the nanoparticles, which is approached by including a new force within the overall force balance. This new force is generated by the substrates.

3.3.2.2. Colloids with Different Sizes. Figure 3-7 shows the schematic diagram for the same silica colloidal particles with different sizes. The experimental condition is the same as for the previous subsection, which was in water at room temperature. Also, as with the previous subsection, the shape of all four silica colloidal particles is assumed to be a spherical one.

The Hamaker constant is not dependent on the size of colloidal particles. The diameters of silica colloidal particles in the figure are assumed to range from 1 μm to 10 nm. This makes us take the first step of the segmental analysis. The van der Waals force is intrinsic for all silica particles, and it is an attractive force. It thus makes an attractive segment for all silica particles. And it is the same regardless of the particle sizes. For a repulsive segment, let us assume that all silica particles are covered with natural surface charges. This is the most likely condition, especially when the solution pH is above 7. The deprotonated surface silanol groups will

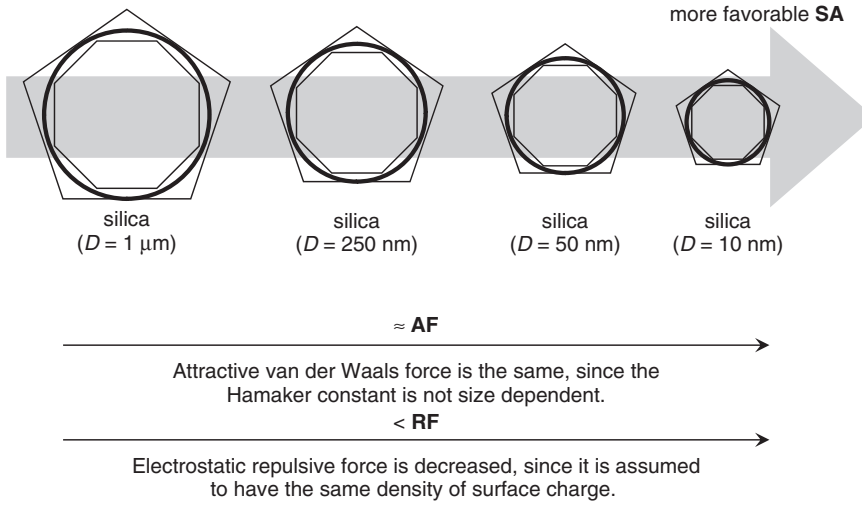

more favorable SA
silica
(D = 1 μm)
silica
(D = 250 nm)
silica
(D = 50 nm)
silica
(D = 10 nm)
≈ AF
Attractive van der Waals force is the same, since the
Hamaker constant is not size dependent.
< RF
Electrostatic repulsive force is decreased, since it is assumed
to have the same density of surface charge.

Figure 3-7. Self-assembly of silica colloidal particles with different sizes in water at room temperature. **SA** is short for self-assembly. **AF** and **RF** refer to attractive and repulsive forces, respectively. *D* is a diameter.

make the surface negatively charged, and their density per unit surface area can be assumed to be nearly the same among the four particles. This suggests that the electrostatic force induced by this surface charge should be their repulsive segment. And this repulsive force will be decreased as the sizes of the particles are decreased. This makes the attractive force remain the same for all silica particles while the repulsive force is decreased as their sizes are decreased. This means that, when there is a self-assembly, it will occur more favorably for the silica particles with smaller sizes.

This analysis of the self-assembly capability of colloidal particles with the same nature but with different sizes can be readily combined with the other analysis from the previous subsection, which was for those of the same size but with different natures. It can help us understand a broader scope of general self-assembly tendencies of different colloidal particles. This will be explored in Figures 7-7 and 7-8 with more details.

Case Study 3.4

The report for the formation of a self-assembled dipolar chain of iron nanoparticles (Butter et al., 2003) provides an interesting example for the general scheme of colloidal self-assembly that is developed here. The self-assembly on that study was performed in an apolar solvent of decalin; thus the electrostatic interaction between the iron nanoparticles can be assumed to be negligible. It also was designed to minimize the effect of the van der Waals attractive force. The only attractive force that can act between the iron nanoparticles is the dipole–dipole interaction. Thus, this is the attractive segment for the iron

nanoparticles. Besides, the surface of the iron nanoparticles is coated with the shell of modified polyisobutene, which generates the isotropic repulsive force between them. Thus it is their repulsive segment. The shell of modified polyisobutene is the same among the iron nanoparticles with different sizes. So the repulsive force among the iron nanoparticles can be assumed to be the same as well. However, as they increased the sizes of the iron nanoparticles, the dipole moments of the nanoparticles also increased rapidly, which resulted in the increase of the dipole–dipole attractive force. As the sizes of the nanoparticles are increased, the attractive force between them is increased accordingly. The system with the smallest iron nanoparticle clearly shows that there is no significant self-assembly, which can be viewed as one of the typical situations of force balance in which the repulsive force is dominant over the attractive force so there can be no self-assembly.

The concept of force balance tells us that, whenever there is an attractive-enough force that can be comparable with this dominant repulsive force, the system should be able to self-assemble through a force balance between the two opposite forces. The experimental data of Butler et al. indeed shows that this is the case for the iron nanoparticles. As the sizes of their iron nanoparticles were increased, they observed an abrupt transition from separate particles to oriented linear aggregates. The oriented linear aggregates are the self-assembled aggregates of their iron nanoparticles whose directionality (linear character) is induced by the directional nature of the dipole–dipole force. And the abrupt transition indicates the point of the force balance, that is, the critical point of self-assembly. This, in this case, could be called *critical particle size*, instead of the typical term, *critical aggregation number* (*can*).

Once a proper segmental analysis is performed, a prediction for self-assembly capability of colloidal particles can be systematically expanded into a two-dimensional general self-assembly diagram. One axis is for their different sizes while the other axis can be assigned to their different natures, such as Hamaker constant. This type of dimensional expansion for the general tendency of self-assembly can be directly applied to the general tendency of nanoassembly. More details on this issue will be described in Chapters 7, 8, and 11.

3.3.3. Directionally Assembling Systems

Now, let us take more complicated self-assembly building units. We will explore the self-assembly of the molecules that have a directional segment. The discussion in this subsection will be nicely contrasted with the one from Section 3.3.1, which was for the molecular self-assembly building units with attractive and repulsive segments only. The identification of the directional segment, its difference compared with the other segments, and its critical role for self-assembly capability will be the main focus in this subsection.

Figure 3-8(a) shows two molecular self-assembly building units. They are octadecanamide, *N*-[4-(-β-*D*-glucopyranosyloxy)phenyl]- and *N*-octadecanoyl-β-*D*-glucopyranosylamine. First, both molecules have a heptadecane hydrocarbon

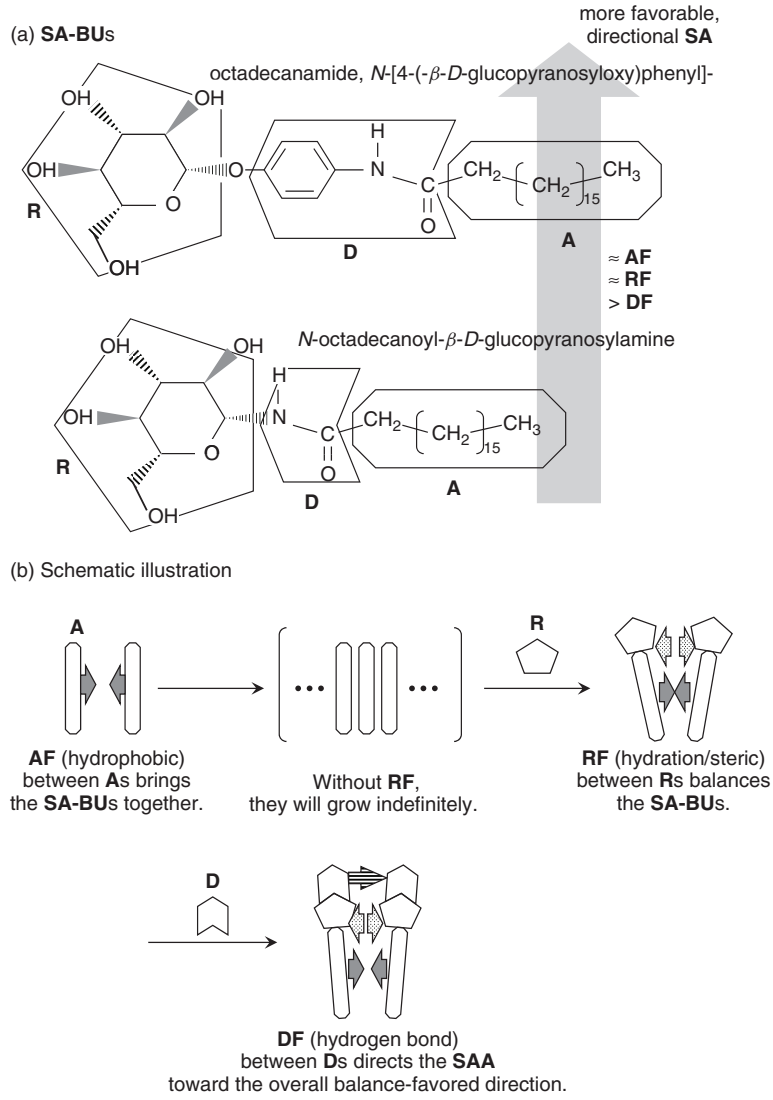


Figure 3-8. Schematic explanation for the self-assembly of molecules that have the combination of attractive (**A**), repulsive (**R**), and directional (**D**) segments. **AF, RF**, and **DF** refer to attractive, repulsive, and directional forces, respectively. **SA, SA-BU**, and **SAA** are short for self-assembly, self-assembly building unit, and self-assembled aggregate, respectively.

chain. It is actually a part of the octadecanoyl chains. But, since the carbonyl group will be assigned as a part of the directional segment shortly, this 17-carbon hydrocarbon chain will be separated from the octadecanoyl chains during segmental analysis. Just like the surfactant molecules that we discussed in Figures 3-3 and 3-4, this long hydrocarbon chain will induce a hydrophobic force in aqueous solution at room temperature. This is an attractive force and is a prime

candidate for the attractive segments for both molecules. The rest of the part for both molecules does not have distinctive parts that can generate solely an attractive force, except for the benzene ring from the molecule above. Hence, it will be reasonable to identify this 17-carbon hydrocarbon chain as an attractive segment for both molecules. In other words, both molecules have the same attractive force.

Turning our attention to the far left-hand side of both molecules, they both have a glucopyranosyl group with exactly the same stereo-characteristics (the same spatial geometry). This is a very bulky group, again spatially, compared with the rest of the part. It thus will be able to generate a significant degree of steric hindrance when they assemble. Even though this group does not have any charged atoms, this steric effect will be repulsive enough to see it as a repulsive force. The tricky part of this assignment is in the four hydroxyl groups. The nature of their spatial configuration makes them contribute to the bulkiness of the glucopyranosyl group. However, the hydroxyl groups will also provide hydrogen bonding when the solvent condition is right. Hydrogen bonding is one of the typical directional forces for self-assembly. At the same time, it can act as an attractive force as well, depending on the solvent and some specific structural nature of the self-assembly building unit. (This aspect will be discussed more intensively in Chapter 5.) But, since it was our intention to have the same spatial configuration for both molecules, any additional role of hydrogen bonding will not be included here. This brings us to the point where this glucopyranosyl group should be assigned as a repulsive segment for both molecules.

For a directional segment, both molecules have an amide group in the middle. An amide group is another typical group that can generate hydrogen bonding. Hydrogen bonding is a directional bonding. Also, since the spatial configuration of this amide group is not much out of the molecular plane, there cannot be much of the steric hindrance between them. These facts should cause the amide group to be assigned as the directional segment for both molecules. For the molecule above, there is one more part to be examined. It is the benzene ring between the amide and glucopyranosyl groups. Because of this specific location, this ring does not have enough room to be spatially active. This means that it does not have much of the repulsive nature. It will rather be able to induce $\pi-\pi$ attractive interaction when the molecules come close together via the action of the hydrophobic attractive force. This will have significant impact and align the molecules into a side-by-side type of packing. A $\pi-\pi$ interaction is relatively weaker force than hydrogen bonding, but it also occurs in a directional manner. This causes us to assign, for the molecule above, the amide group combined with the benzene ring as a directional segment, but with quite a strong sense of attractive force.

More details regarding this discussion will be presented in the next subsection. However, for these two molecules, the segmental analysis we just established provides a tool to estimate their self-assembly capability and its general tendency. Both have the same attractive and repulsive segments. As for the directional force, however, the molecule above can be considered as having more directional force. The amide group and the benzene ring within the directional segment will direct the self-assembly process cooperatively, but with an additional sense of attractive force.

This gives us enough of an argument to conclude that both molecules have satisfactory segmental structure to self-assemble in solution and the molecule above will self-assemble more favorably. It can be stated that both molecules will experience directional self-assembly. But the one above will be more directional. Literature results show that both molecules form a well-developed nanotubular type of self-assembled aggregate in aqueous-based solution (Shimizu et al., 2005). Nanotubular structure is one of the typical structures that are assembled through a directional self-assembly. Also, the results show that the nanotube from the molecule above generally has longer length in its long axis, which should be the case based on the segmental analysis we have performed in this subsection. The one above has a more directional segment than the one below, while the other two segments (the attractive and repulsive ones) are exactly the same.

Figure 3-8(b) shows a schematic explanation of the self-assembly of building units with a directional segment. As always, for the right segmental analysis, our first attention should be on an attractive segment. For both self-assembly building units shown in Figure 3-8(a), the attractive segment is the hydrocarbon chain. At the initial stage of self-assembly, this segment will bring the self-assembly building units together through its attractive hydrophobic force. If we assume that there is no repulsive force acting during this process, these self-assembly building units will keep aggregating indefinitely. This is when the repulsive segment should come into play. The bulky repulsive segment for these self-assembly building units begins to counterbalance the action of the attractive force. In this particular case, it will be through the steric effect. This second stage of the process eventually will reach the point of balance between the two opposite forces. Meanwhile, these self-assembly building units have a third segment, which is the directional segment. It is at this third stage where this directional segment should be included in the picture of the self-assembly process. Through hydrogen bonding between neighboring self-assembly building units, this segment can determine the direction of the self-assembly process. It can also reinforce the action of the attractive segment. The entire self-assembly process now takes place through the balance between these three different types of forces. And their balance will be reached at a certain point of the process that will be reflected by self-assembly parameters such as *cmc*. The directionality in the structure of the self-assembled aggregates will be also determined by the direction that is favored by the force balance. More details on this aspect will be described in Chapter 5.

As the simple segmental analysis from the above subsections helped clarify the self-assembly processes of the surfactant molecules and the prediction of their self-assembly parameters, this segmental analysis for the self-assembly building units with a directional segment also helps explain a vast majority of the potential self-assembly building units that have any type of directional segment. Directional segments are not limited to the groups that induce hydrogen bonding or $\pi-\pi$ interaction. There are many other types of forces that can act as a directional force, and in many cases they work in a cooperative manner. However, whatever the actual directional force situation might be, what matters is to get the proper segmental picture through the analysis of their molecular structures. Once this is

properly preformed, the rest of the analysis for their self-assembly is almost routine. And the prediction of related self-assembly parameters can be made accordingly by using a reference self-assembly system.

If we assume, just for the sake of explanation, that the surfactant molecules are somewhat traditional types of self-assembly building units that have been around for a long time, the self-assembly building units shown in this subsection that have the third structural feature (directional segments) could be viewed as a new type of self-assembly building units. As biological studies go into the molecular level, new discoveries regarding the biological functions that are related to the assembly of these types of self-assembly building units (with certain types of directional segments) continue to be made. Not only their assembled structures but their functions as well are affected by this directional segment. Biotechnology, somewhat inevitably, develops a variety of bio-mimetic systems, and as a result there are many unique bio-mimetic self-assembly building units available now. Sugar group–based amphiphiles and functionally modified lipid molecules are just a few examples. The concept of segmental analysis can provide a facile tool to understand and track the self-assembly processes of those novel molecules.

3.3.4. Self-Assembly at Surfaces

This subsection examines the self-assembly of molecular self-assembly building units at surfaces. Two distinctive types of surfaces are under consideration: hydrophobic and hydrophilic surfaces. There are many different types of surfaces that have capability as a substrate for self-assembly. However, since these two are the most representative ones, a proper examination of self-assembly on them can provide a good foundation for a general understanding of self-assembly on different surfaces. The main discussion is limited to molecular self-assembly building units. But it can be readily expanded for other types of building units as well. The work that reports a possible critical aggregation number for the self-assembly of gold nanoparticles at liquid–liquid interface is interesting to read in this regard (Sanyal et al., 2008). A theoretical work that describes the self-assembly of colloidal particles at liquid surfaces with competing interaction between an attractive force and a repulsive force is also valuable (Archer, 2008).

One of the most prominent differences between self-assembly at surfaces and that in bulk solutions is the unique role of surfaces in the balance of forces. Unless the interaction of the self-assembly building unit with the surface is strong (for example, chemisorption or complexation), the surface generates the interaction comparable to typical intermolecular and colloidal forces. This means that this interaction becomes another important player during the process of force balance for self-assembly. It sometimes provides an additional attractive force. It often induces a unique directional force since a surface can direct self-assembly along its direction.

The first step is the proper segmental analysis of building units. Figure 3-9(a) presents the self-assembly building unit that is considered in this subsection. It also shows two different types of surfaces. The cationic surfactant molecule,

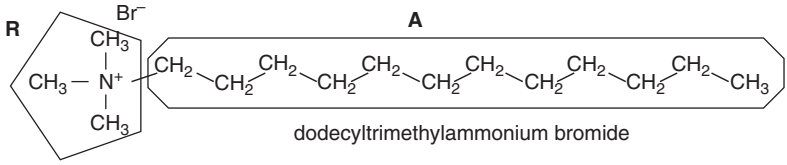
dodecyltrimethylammonium bromide, has been analyzed for self-assembly in bulk solutions in the previous subsections; thus it will provide a nice opportunity to compare the similarities and differences between self-assembly in bulk solutions and at surfaces. Cases I and II in the figure are for hydrophobic and hydrophilic surfaces, respectively. The bold thick line is used for them. Typical examples of hydrophobic surfaces include silica, silicon, polystyrene, and metal that are hydrophobitized. Most of the oil surfaces are hydrophobic, too. Simply speaking, these surfaces repel water molecules while attracting nonpolar substances. When solid surfaces such as silica, silicon, polystyrene, and metal are charged or hydroxylated, they become hydrophilic. Surfaces of water and aqueous-based liquids are hydrophilic, too. They usually have a positive affinity with polar substances.

A segmental analysis for dodecyltrimethylammonium bromide has been done in Figure 3-2. The dodecyl hydrocarbon chain is its attractive segment, which will induce an attractive hydrophobic force. The trimethylammonium group is its repulsive segment. Details for the surfaces will be shown in the following subsections.

3.3.4.1. Hydrophobic Surfaces. Figure 3-9(b) shows a schematic analysis for the self-assembly of cationic surfactants on hydrophobic surfaces. Figure 3-9(c) has a general tendency that can be developed from it. This is for case I of Figure 3-9(a).

Surfaces that have a hydrophobic nature have a natural tendency to attract nonpolar molecules. The strength of this interaction is dependent on the hydrophobicity of the surfaces. This implies that hydrophobic surfaces have a stronger affinity with the hydrocarbon chain of cationic surfactant than its trimethylammonium group. The hydrocarbon chain is the attractive segment for the cationic surfactant. This suggests that the interaction of the attractive segment with the surface has to be considered first. Figure 3-9(b) starts with this observation. First, the attractive segment of the surfactant molecule is attracted on the surface. This is through hydrophobic force. As more attractive segments come to the surface, an attractive hydrophobic force between them acts to bring the surfactant molecule (self-assembly building unit) together on the surface. If it is assumed that there is no repulsive force that can counterbalance this attractive process, the self-assembly building units will keep aggregating (on the surface) until either they are completly depleted from the source or the surface runs out of its available space for the assembly. This is when a repulsive segment should come into play. The repulsive segment that induces an electrostatic force in this case begins to repel the self-assembly building units. This counterbalancing is continued until the interaction between these two opposite forces is balanced. This balance is a thermodynamic equilibrium. Building units from above the surface have a whole degree of freedom to be freely exchanged with those within self-assembled aggregates on the surface, and vice versa. The last step is to define the role of the surface during its interaction with the building units. First, it has acted as an attractive segment of its own. In other words, it was the major driving force that brought the building units to the surface. But this role as an attractive segment also has caused the self-assembly process to be directional. As long as the interaction of the surface with the building units is comparable to

(a) **SA-BU** and conditions



dodecyltrimethylammonium bromide

surface/interface

For case I:

1. Solid surfaces such as silica, silicon, polystyrene, and metal that are hydrophobitized
2. Oil surfaces

surface/interface

For case II:

1. Solid surfaces such as silica, silicon, polystyrene, and metal that are charged or hydroxylated
2. Water surface

(b) Schematic illustration for case I:

When **A** has stronger affinity with the surface than **R**

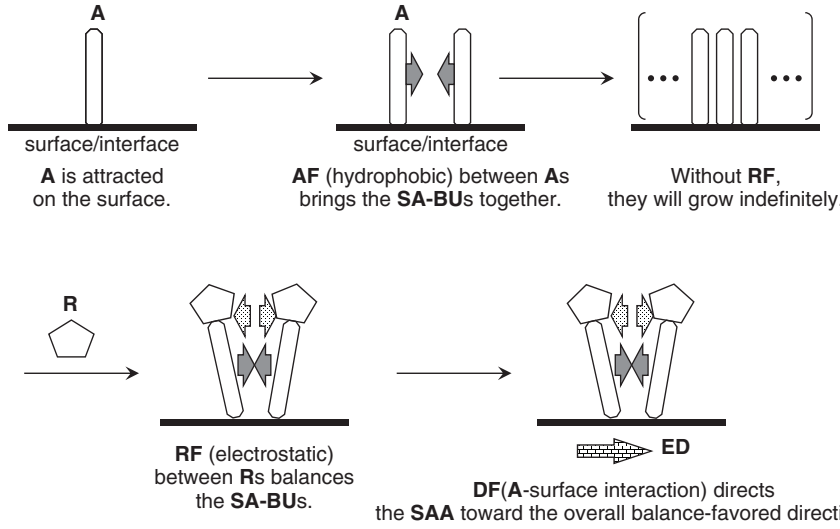
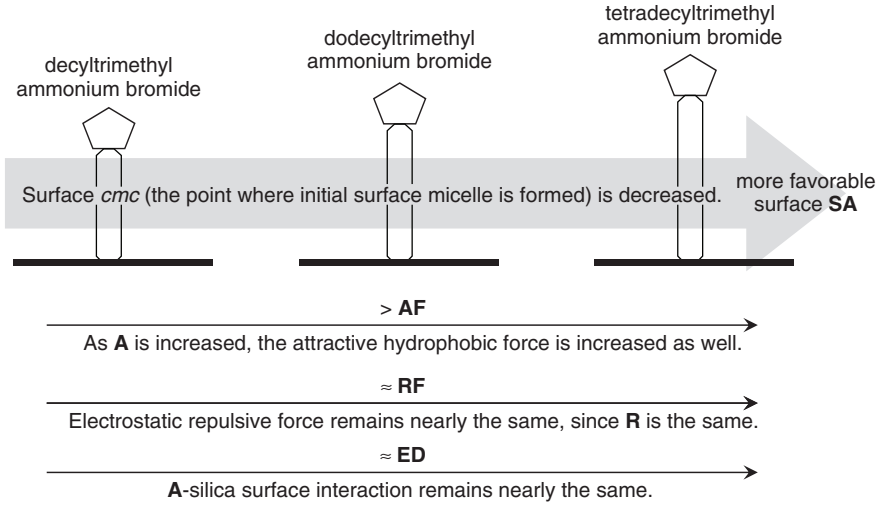


Figure 3-9. Schematic explanation for the surface self-assembly of a molecule that has the combination of attractive (**A**) and repulsive (**R**) segments. **AF, RF**, and **DF** refer to attractive, repulsive, and directional forces, respectively. **SA, SA-BU**, and **SAA** are short for self-assembly, self-assembly building unit, and self-assembled aggregate, respectively. **ED** is external force–induced directional factor. *cmc* is critical micellar concentration.

(c) Case I study :

Surface self-assembly of alkyl trimethyl ammonium bromides
at octadecyltrichlorosilane-modified silica surface in water at room temperature


decyltrimethyl ammonium bromide
dodecyltrimethyl ammonium bromide
tetradecyltrimethyl ammonium bromide
Surface *cmc* (the point where initial surface micelle is formed) is decreased.
more favorable surface **SA**
> **AF**
As **A** is increased, the attractive hydrophobic force is increased as well.
≈ **RF**
Electrostatic repulsive force remains nearly the same, since **R** is the same.
≈ **ED**
A-silica surface interaction remains nearly the same.

(d) Schematic illustration for case II:

When **R** has stronger affinity with the surface than **A**

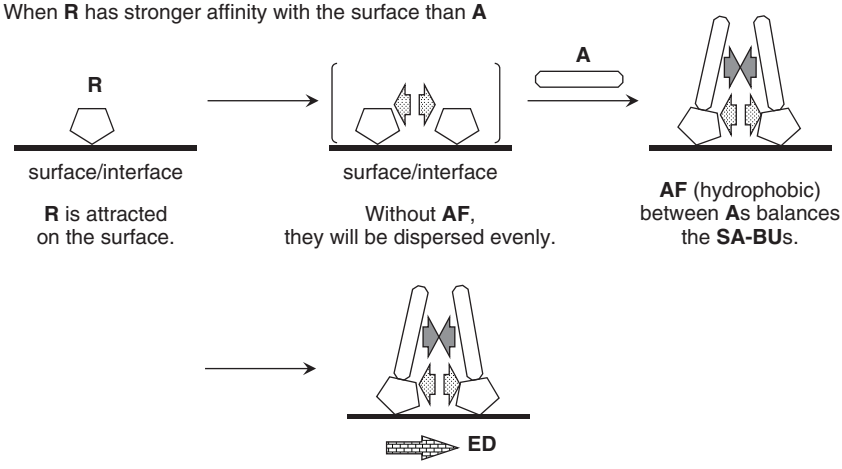

R
A
surface/interface
surface/interface
R is attracted on the surface.
Without **AF**, they will be dispersed evenly.
AF (hydrophobic) between **A**s balances the **SA-BU**s.
ED
DF (**R**-surface interaction) directs the **SAA** toward the overall balance-favored direction.

Figure 3-9. (*Continued*)

(e) Case II study:

Surface self-assembly of alkyl trimethyl ammonium bromides
at surface-hydroxylated silica surface in water at room temperature at high pH

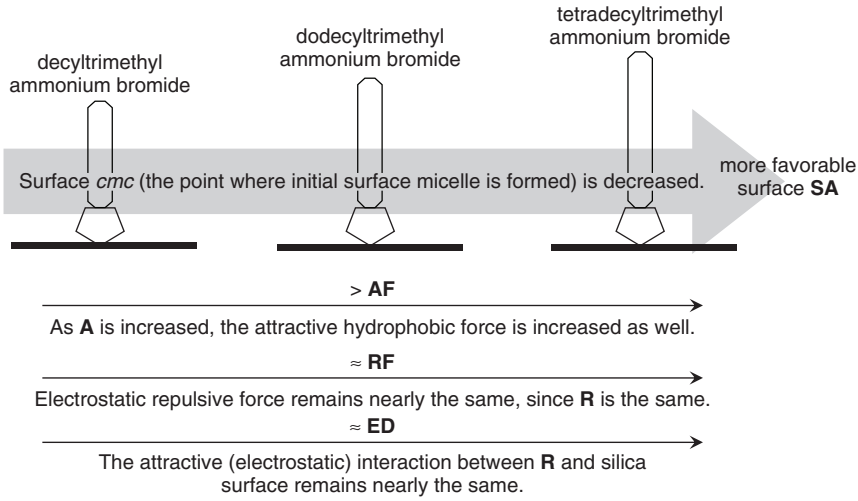

decyltrimethyl ammonium bromide
dodecyltrimethyl ammonium bromide
tetradecyltrimethyl ammonium bromide
Surface *cmc* (the point where initial surface micelle is formed) is decreased.
more favorable surface **SA**
> **AF**
As **A** is increased, the attractive hydrophobic force is increased as well.
≈ **RF**
Electrostatic repulsive force remains nearly the same, since **R** is the same.
≈ **ED**
The attractive (electrostatic) interaction between **R** and silica surface remains nearly the same.

Figure 3-9. (*Continued*)

the other forces that are involved during this process, this interaction also acts as a directional force that determines the direction of the entire self-assembly process.

This schematic illustration is based on the upright mode of self-assembly building unit; that is, the head group (trimethylammonium) is far away from the surface. However, the basic principle behind this is the same as for the other packing situation: the lying-down mode. The self-assembly in the lying-down mode can also be tracked by this segmental analysis. In lying-down mode, both segments are attracted to the surface.

Now let us take a look at some specific examples. Figure 3-9(c) shows the self-assembly of three alkyltrimethylammonium bromide homologue series on hydrophobic surfaces. The three building units are decyl-, dodecyl-, and tetradecyltrimethylammonium bromides. They have the same head group (trimethylammonium), which should be assigned as their repulsive segment. The difference is in the length of their hydrocarbon chains. The hydrocarbon chains should be assigned as their attractive segments, but its strength is increased as the length is increased. The surface that is under consideration is silica, whose uppermost layer is modified with the self-assembled monolayer of octadecyltrichlorosilane. This modification causes the silica surface to be coated with methyl groups, and thus provides a hydrophobic nature for it. The experimental condition is in water at room temperature, just as for the self-assemblies in the previous subsections. With the assumption of an upright mode, which, by the way, is proven to be a reasonable one by literature results, the segmental analysis is as follows. The attractive hydrophobic force should be increased as the hydrocarbon chain

length is increased. The repulsive force, on the other hand, should remain nearly the same. The electrostatic repulsive force between the positively charged nitrogen atoms has no reason to be significantly different among these three building units. The directional force that is induced by the surface should also be nearly the same. This external force–induced directional factor (see Figure 1-5 for more about this) is nothing but the hydrophobic interaction between the hydrocarbon chains and the surface. The charged head group does not have much power to affect this interaction. And the overall direction of the self-assembly induced by the surface will always be the direction of the surface itself. Overall, this analysis shows that, as the hydrocarbon chain length is increased, (1) the attractive force is increased, (2) the repulsive force is the same, and (3) the directional force is the same. Literature results confirm that decyltrimethylammonium bromide self-assembles on this particular type of hydrophobic surface at room temperature in water, and forms a self-assembled aggregate called *hemimicelle*. This can make it a reference self-assembly system for this set of examples. The segmental analysis we have tells us that the rest of the two building units will also self-assemble at the same conditions. The favorability of self-assembly will be increased as the hydrocarbon chain length is increased. With the analogy of *cmc* in bulk solutions, the point where the initial hemimicelle is formed, that is, the point where the two opposite forces are balanced, can be evidenced by the value of surface *cmc*. This value should be decreased as the hydrocarbon chain length is increased.

This generalized scheme and subsequent examples using a typical homologue series of cationic surfactant can be expanded for similar self-assembly systems. As long as the segmental analysis is similar, and as long as the surface is hydrophobic, the same general tendency for their self-assembly should be anticipated. As with similar self-assembly systems in bulk solutions, once a proper reference system with well-known self-assembly parameters is identified, the values of self-assembly parameters for the rest of the self-assembly systems can be predicted almost in a semiquantitative way.

Case Study 3.5

There is an article (Du et al., 2009) that reports an actual experimental example that is comparable to this generalized scheme. Self-assembly of the alkylsiloxane homologue series on the surface of a polyimide substrate shows a dramatic impact of increased hydrophobic interaction on their self-assembled aggregates. As the length of their alkyl chain (attractive segment) is increased from decyl to hexadecyl, the hydrophobic attractive force between them is increased accordingly. What is more interesting for this study is that the surface of the polyimide substrate is mechanically rubbed so that its alkyl moieties are elongated along the direction of the rubbing. This ensures the hydrophobic attractive interaction between the building units (alkylsiloxanes) and the surface, which also is increased as the alkyl chain length of the building unit is increased. This feature also works to direct the self-assembly by determining the direction of the first layer of building units on the surface. Thus, this is the external force–induced directional factor for this system. These particular building units do not have an

intrinsic repulsive segment. The tris(trimethoxysilyloxy)silane group becomes reactive when it is hydrolyzed. But with the sense that it, too, contributes to the attractive process, it is more logical to classify it as a part of the attractive segment. Figure 11-2(a) will show more details about this type of segmental analysis.

Since the self-assembled aggregates are prepared by dip-coating of the sol followed by drying, the concentration of the building units should keep increasing until the final films are formed. This is an ideal condition for multi-step self-assembly, which can promote the formation of a liquid crystal type of self-assembled aggregates. The full scope of the multi-step self-assembly will be presented in Chapter 4. The attractive interaction is balanced by the defined area of the substrate. Therefore, the segmental analysis for this self-assembly system is that the building unit with the hexadecyl chain has more attractive force, not only between the building units but with the surface as well, than the one with the decyl chain. The results of Du et al. show that the hexagonal morphology of self-assembled aggregate (with clearly defined directionality) is formed for the building unit with the decyl chain while the lamellar one (also with clearly defined directionality) is formed for the one with the hexadecyl chain. This can be well understood within the logic of the segmental analysis. Even though it does not predict those hexagonal and lamellar morphologies up front, once we have this analysis along with the experimental results from the two building units, the predictions of the self-assembly and its outcome from the other members of the homologue series become very straightforward.

3.3.4.2. Hydrophilic Surfaces. Figures 3-9(d) and (e) are for case II in Figure 3-9(a). These are with the same cationic surfactants but on hydrophilic surfaces.

Figure 3-9(d) shows the schematic illustration. The surface where self-assembly takes place is now hydrophilic. Hydrophilic surfaces have a higher affinity with polar substances. Cationic surfactant molecules consist of one nonpolar attractive segment and one polar repulsive segment. This simply indicates that the repulsive segment of a cationic surfactant molecule should have a higher affinity with a hydrophilic surface than the attractive segment. Thus, the repulsive segment should be attracted to the surface first. This happens through an electrostatic attractive force if the surface is negatively charged. This situation is exactly the opposite of case I. If we assume, at this step, that the surfactant molecules have no attractive segment, then they will be simply dispersed evenly on the surface. This is not a self-assembly. There will be no clear boundary of molecular aggregation of any kind. The next step is where the attractive segment is included. The attractive segment induces an attractive hydrophobic force. This force will bring the molecules together, and eventually be balanced with the repulsive force. As in case I, this balance is a thermodynamic equilibrium. Surfactant molecules (self-assembly building units) from above the surface can be freely exchanged with those within self-assembled aggregates on the surface, and vice versa. The last step is to include the role of the surface. It has already been shown that a part of

the surface has acted as an attractive segment of its own, which has contributed to attracting the repulsive segment of the surfactant molecules. As long as this interaction is strong enough to hold the whole surfactant molecules on the surface with a time scale slower than the one for the dynamics of the self-assembled aggregates, the surface inevitably will direct the self-assembly process along its own direction.

As in case I, this schematic illustration is based on the upright mode. The hydrocarbon chain is away from the surface. However, the basic principle is the same as for the lying-down mode. Usually, the chemical characteristics of self-assembly building units determine their molecular configuration during surface self-assembly. But certain self-assembly building units have the flexibility to be either of the modes depending on experimental conditions.

The example surface for case II is silica whose surface is modified with a hydroxyl group. The condition is in water at room temperature with high solution pH. This will force the silica surface to be negatively charged. The same homologue series of cationic surfactant as in the previous subsection is chosen for self-assembly building units. Figure 3-9(e) shows the general tendency of their surface self-assembly. The three cationic surfactants under consideration are decyl-, dodecyl-, and tetradecyltrimethylammonium bromides. The segmental analysis for them has already been performed. The hydrocarbon chains are their attractive segment, and the trimethylammonium group is their repulsive segment. The attractive force should be increased as the hydrocarbon chain length is increased. The repulsive segments are the same and will generate an electrostatic repulsive force. The same molecular structure of repulsive segments does not necessarily guarantee the same repulsive force between them. However, under the usual experimental conditions, it will be reasonable to expect that the repulsive force is nearly the same for the three building units. It thus will be safe to assume that the electrostatic repulsive forces between the repulsive segments are the same, despite the fact that the repulsive segments are also interacting with the surface of silica through an electrostatic attractive force. The directional force here is the interaction of the surface with the repulsive segments of the building units. There is no reason that this cannot be nearly the same for the three building units. All the experimental conditions are the same and the possible impact of the different lengths of the hydrocarbon chains should be minimal.

The general self-assembly trend for case II is the same as for case I. As the hydrocarbon chain length is increased, the attractive force is increased while the rest of the two forces (the repulsive and directional ones) remain the same. As a result, the surface self-assembly occurs more favorably when its building unit has a longer hydrocarbon chain. The surface *cmc* is decreased accordingly. For case I, the self-assembled aggregates were hemimicelle. For case II, on the contrary, the head group is directly in contact with the surface. The self-assembled aggregates thus have a full circular shape in cross-section when viewed through the direction of the surface, even though there is a possibility that the shape might have been distorted to some degree because of the interaction with the surface. This is called *semimicelle*.

3.4. COLLECTION OF PRIMARY SELF-ASSEMBLED AGGREGATES

Table 3-1 lists the collection of self-assembled aggregates. They are primary self-assembled aggregates, which means that they are the aggregates that appear first when each of the self-assembly building units self-assembles. Some of the aggregates that are usually formed in solution can be formed at surfaces, too. But those that are referred as a result of surface self-assembly are almost solely formed on surfaces. The collection of higher-order self-assembled aggregates will be presented in Section 4.4.

The names of each of the aggregates are those that appear the most often in the literature. Some articles tend to use somewhat different names even though they indicate the same systems. The brief description for each aggregate should be helpful to clarify it. Otherwise, whenever one of these names appears, it is safe to assume that it is a primary self-assembled aggregate. Table 3-1 also presents the segment combination and kind of self-assembly building unit with which each aggregate is most likely formed. Cross-referencing with the self-assembly building units shown in Section 1.5 can help clarify why a certain form of aggregate is the one most likely to appear for a certain type of building unit. This in turn can help in designing nanotechnology systems. For example, *micelle* is referred to as a spherical aggregation with discrete size and shape. It can be formed from the different kinds of building units that have the combination of attractive and repulsive segments. This can guide us in that, when designing nanotechnology systems that need a spherical morphology with a nanometer scale, there can be different options to use. Not only molecular building units, but polymeric, biological, and bio-mimetic building units can be used for this as well. Different sizes of building units can be used as long as they have the attractive and repulsive segments, which indicates that the sizes of the nanoscale morphologies can be tuned. Building units with different natures can be used also as long as they have the attractive and repulsive segments, which indicates that the physical and chemical characteristics of the nanoscale morphologies can be designed as well.

3.5. SUMMARY

This chapter addressed the first key questions regarding the design of self-assembly systems. These were:

1. Will your self-assembly building units actually self-assemble?
2. Why do they self-assemble?
3. How do we identify it?

We have seen that these questions can be reasonably answered by carefully analyzing the structures of each self-assembly building unit and their relationships. The discussion was quite straightforward and systematic, and practical for a wide range of self-assembly building units. In addition, it was useful for self-assembly both in solutions and at surfaces.

TABLE 3-1. Collection of primary self-assembled aggregates, a brief description of each of them, and the segment combination and kind of building units with which each self-assembled aggregate is most likely formed. m, c, p, b, b-m indicate molecular, colloidal, polymeric, biological, and bio-mimetic building units, respectively. A, R, R^c, and D^c refer to attractive, repulsive, conditional repulsive, and conditional directional segments, respectively. seg. com. and surf. are short for segment combination and surfactant, respectively.

		Building Unit	
Name	Description	Seg. Com.	Kind
micelle	spherical aggregation in solution with discrete size and shape	any one with **A** and **R**	m, p, b, b-m
bicelle	bilayered mixed micelle	any one with **A** and **R**	m, p, b, b-m
reverse micelle	spherical aggregate in solution with water droplet inside	any one with **A** and **R**	m, p, b, b-m
microemulsion	spherical water or oil droplet thermodynamically stabilized by building units	any one with **A** and **R**	m, p, b, b-m
macroemulsion	water or oil droplet kinetically stabilized by building units	any one with **A** and **R**	m, p, b, b-m
double emulsion	water or oil droplet and thin layer stabilized by building units	any one with **A** and **R**	m, p, b, b-m
vesicle	spherical bilayer hollow sphere	any one with **A** and **R**	m, p, b, b-m
liposome	spherical bilayer hollow sphere	lipids with **A** and **R**	b, b-m
noisome	vesicle of nonionic surf.	surf. with **A** and **R**	m
foam	air or gas bubble stabilized by building unit monolayer	any one with **A** and **R**	m, p
black film	thin liquid layer stabilized by building units	any one with **A** and **R**	m
self-assembled monolayer[a]	monolayer of building units chemisorbed on solid surface	any one with **A** and $\mathbf{D}^c$	m, p, b, b-m
Langmuir monolayer[a]	monolayer of building unit stabilized on liquid surface	any one with **A** and **R**	m, c, p, b, b-m
Langmuir-Blodgett (LB) monolayer[a]	Langmuir monolayer transferred on solid surface	any one with **A** and **R**	m, c, p, b, b-m
epitaxial adlayer[a]	adlayer on solid surface deposited through epitaxial matching	any one with **A** and $\mathbf{R}^c$	m
vapor deposited film[a]	monolayer deposited by vapor deposition	any one with **A**	m, b, b-m
hemimicelle[a]	hemispherical aggregate on solid surface	any one with **A** and **R**	m
semimicelle[a]	spherical aggregate on solid surface	any one with **A** and **R**	m
surface micelle[a]	2D micelle on liquid surface	any one with **A** and **R**	m
colloidal cluster	aggregates of colloidal particles in solution	any one with **A** and **R**	c
colloidal monolayer[a]	monolayer of colloidal particles on solid surface	any one with **A** and **R**	c

[a]Self-assembled aggregates formed as a result of surface self-assembly. All the others are formed via self-assembly in solutions.

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4

Identification of Multi-Step Self-Assemblies

4.1. ASSEMBLY ISSUE

This chapter discusses the capability of self-assembly building units for the higher-orders of self-assembly processes. For many self-assembly building units, their self-assembly processes do not stop as the initial self-assembled aggregates are formed. As long as the condition is right, their self-assembly processes can continue to occur even after the formation of their initial self-assembled aggregates. This phenomenon is called *higher-order self-assembly processes*. The self-assembly that forms the initial aggregate is primary self-assembly. After that, each step of self-assembly is called secondary self-assembly, tertiary self-assembly, and so forth. In the previous chapter we asked the most fundamental question for self-assembly systems: whether a given self-assembly building unit will self-assemble. In this chapter we will address the next question:

> *Will a given self-assembly building unit proceed toward higher-order self-assembly processes in a given experimental condition?*

This question can be rephrased as:

> *Does the self-assembly building unit have the capability of multi-step self-assembly?*

It was shown in the previous chapter that the structural analysis of self-assembly building units (*segmental analysis*—see Subsection 1.2.2 for details) was a useful

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means to determine the self-assembly capability of different building units. This chapter shows that, once the answer for the first question is yes (that a given building unit self-assembled under a given condition), the same concept is used to address the second question—to determine whether the building unit has the capability of multi-step self-assembly. What is necessary is the expansion of the concept of segmental analysis.

4.2. GENERAL OVERVIEW

Figure 4-1 presents a general overview of the identification of the multi-step self-assembly capability. The self-assembly building units here are those that are already confirmed to have the self-assembly capability under a given condition. The procedure is exactly the same as the one in Figure 3-1, whose main purpose was to test whether a building unit that appears to have the self-assembly capability can indeed self-assemble under a given condition. For Figure 4-1, the main purpose is to test whether the self-assembled aggregate (primary self-assembled aggregate) of that building unit that is proven to self-assemble will continue toward the next steps of the self-assembly process. Thus, both figures have an almost identical structure. An

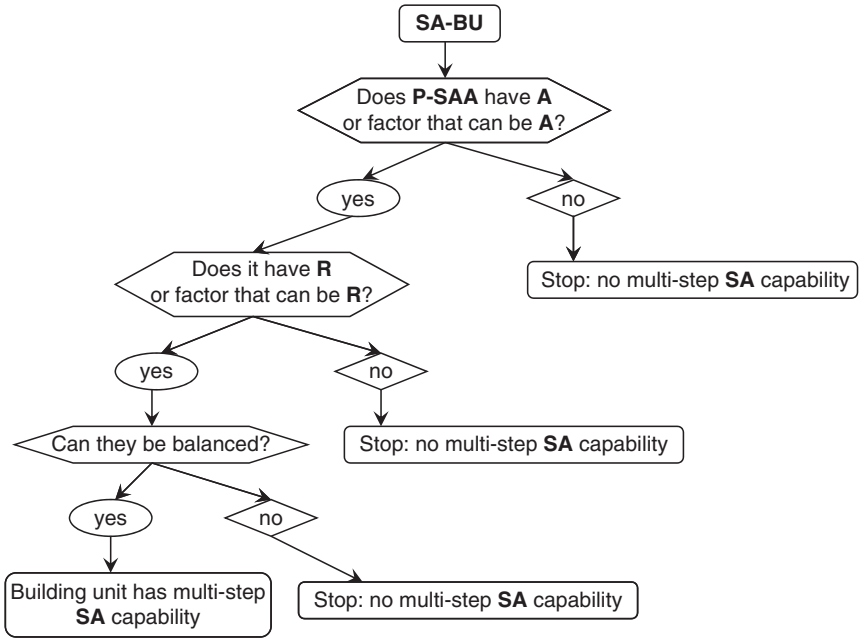


Figure 4-1. General overview of the identification of the multi-step self-assembly capability of a given self-assembly building unit (**SA-BU**). **A** and **R** refer to attractive and repulsive segments, respectively. **SA** and **P-SAA** are short for self-assembly and primary self-assembled aggregate, respectively.

important difference is that what has to be considered now in terms of segmental analysis (see Subsection 1.2.2 for details) is the primary self-assembled aggregate instead of the self-assembly building unit. This is about the primary self-assembled aggregates and their self-assembly processes. The key is how to perform segmental analysis for the primary self-assembled aggregates.

Once a self-assembly building unit is confirmed to have capability for self-assembly under a given condition, then the question to ask first is whether the primary self-assembled aggregate has an attractive segment. For the self-assembly of primary aggregates, in many cases, environmental conditions can have a critical influence. Thus, the question to ask here also includes whether the primary aggregate has a factor that can act as an attractive segment under a given condition. If the answers for both questions are no, then it is certain that the primary aggregate does not have multi-step self-assembly capability. In other words, this means that the building unit will stop its apparent self-assembly as it forms the primary aggregates. If, however, the answer for either one of the questions is yes (that it has an attractive segment and/or a factor to make it one), then the next question should be whether the primary aggregate has a repulsive segment. Once again, for the same reason that experimental conditions can critically affect the self-assembly of the primary aggregates, the question is also whether it has a factor that can act as a repulsive segment under a given condition. If the answers for both questions are no, then it will be safe to say that the primary aggregate has no definitive capability for multi-step self-assembly processes. If, however, the answer is yes for either one of these questions, which means that the primary aggregate has the two basic segments for self-assembly (attractive and repulsive segments), the final question to ask is whether the interaction between the two segments can be balanced under a given condition. If the answer is no, then the primary aggregate has no capability for multi-step self-assembly. If the attractive segment overwhelms the repulsive one, the primary aggregates will be simply precipitated out. If the segmental structure has the opposite effect and it overwhelms the repulsive segment, then they will stay stable. If the answer is yes, which means that the two opposite forces are balanced under a given condition, then the primary aggregates will continue to assemble until they reach the point of force balance. This is a self-assembly as defined in Chapter 1. It occurs after the apparent completion of the self-assembly that forms the primary aggregate. Therefore, it is a secondary self-assembly process continuing from the prior self-assembly process (primary self-assembly). It now can be concluded that the primary aggregate has the capability of multi-step self-assembly.

A proper structural analysis of the primary aggregate is necessary to determine its segmental structure. However, the primary self-assembly building unit itself provides a wealth of information for this, too. The first clue can be found from its molecular or colloidal structure. This will be discussed in more detail in Chapters 5 and 6. The second one comes from the experimental conditions where the self-assembly takes place. The most common conditions are the concentration of the building unit, any conditions that can significantly change any of the forces involved, and any conditions that can change all of them together. Whatever the

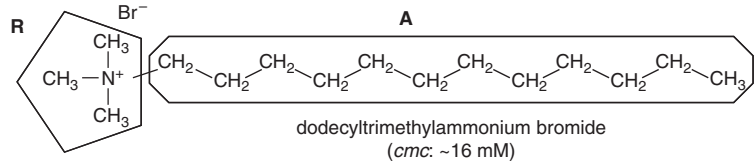
actual situation for a given self-assembly system might be, the system will go through the whole rebalance of all the forces involved. And whenever this is satisfied within the criteria of the process in Figure 4-1, it can be concluded that the building unit has the capability of multi-step self-assembly. This is the secondary self-assembly and the secondary self-assembled aggregate is formed. This secondary aggregate is the tertiary self-assembly building unit if there is another step of self-assembly after the secondary self-assembly. The same concept of segmental analysis can be applied to test the self-assembly capability of the tertiary building unit.

4.3. ASSEMBLY PRINCIPLES

This section shows the two representative examples of self-assembly systems that can continue their self-assembly processes after the apparent completion of the primary self-assembly. The first one is for a molecular self-assembly system and the second one is for a colloidal self-assembly system. For both examples, building units consist of only two fundamental segments (attractive and repulsive segments). Also, for both examples, both segments of the primary aggregates are acquired from experimental conditions. The rich examples where the attractive and repulsive segments of the primary aggregates are acquired by the intrinsic structures of their building units (primary) are found in bio-mimetic and biological building units. In many cases, these attractive and repulsive segments of the primary aggregates are hidden by (or buried into) the attractive and repulsive segments of the building units (primary). Once the primary self-assembly is apparently completed, which means the primary aggregates are formed, the attractive and repulsive segments (also, in many cases, the directional segment and others as well) for the primary aggregates are exposed (or activated). Also, for many bio-mimetic and biological self-assembly systems, this exposing (or activating) of new segments is continued to the point where the self-assembled aggregates acquire length scales way beyond (many orders of higher magnitude) the length scales of their primary building units. The sizes of the primary self-assembly building units are usually within the nanometer scale. However, it is not uncommon that the final forms of the self-assembled aggregates that are formed after a series of multi-step self-assembly processes have their sizes over the millimeter scale.

There is an article (Smith, 2006) that reviews the hierarchical self-assembly of supramolecular dendrimers. Another article (Goodby et al., 2009) shows the self-assembly of the nanoparticles into secondary and tertiary hierarchical structures. The building units and assembly systems for these two reports are somewhat complicated, but they follow the principles of the hierarchical self-assembly that are presented in this section. The work by Rao et al. (2010) that presents the hierarchical self-assembly of a donor–acceptor non-covalent amphiphilic pair into supramolecular hydrogel and nanofiber is also worth reading in this regard.

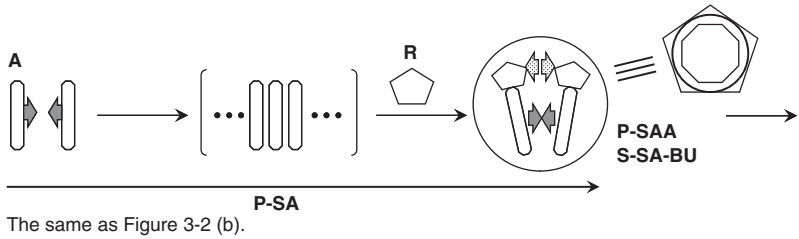
(a) **SA-BU** and **SA** conditions



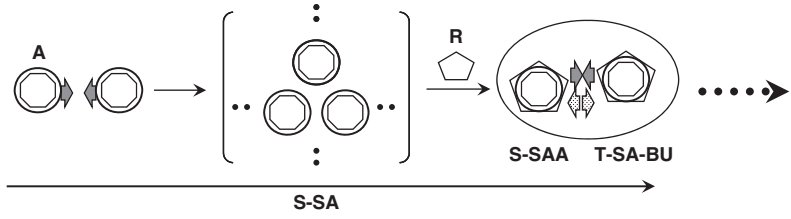
Conditions for the change of **AF** and/or **RF**:

1. Salt (counterion): potassium bromide (KBr)
2. Concentration of dodecyltrimethylammonium bromide

(b) Schematic illustration



The same as Figure 3-2 (b).



The same as Figure 3-5 (b).

Figure 4-2. Schematic explanation of the multi-step self-assembly of a molecule that has the combination of attractive (**A**) and repulsive (**R**) segments. **AF** and **RF** refer to attractive and repulsive forces, respectively. **SA, P-SA**, and **S-SA** are short for self-assembly, primary self-assembly, and secondary self-assembly, respectively. **SA-BU, S-SA-BU**, and **T-SA-BU** are short for self-assembly building unit, secondary self-assembly building unit, and tertiary self-assembly building unit, respectively. **P-SAA** and **S-SAA** are short for primary and secondary self-assembled aggregates, respectively.

4.3.1. Molecular Self-Assembly of Surfactants

Figure 4-2(a) shows the self-assembly building unit and the conditions that will be considered for multi-step self-assembly. As indicated in the previous paragraph, this is the case of a molecular self-assembly whose building unit has the attractive and repulsive segments only.

The self-assembly building unit is dodecyltrimethylammonium bromide. Its segmental analysis was performed in Figure 3-2(a). The long hydrocarbon chain is an attractive segment because this part induces an attractive hydrophobic force. The trimethylammonium part is a repulsive segment because it generates an electrostatic repulsive force by the action of the negatively charged nitrogen atom. The condition that can make this analysis practical is in water at room temperature. Its *cmc* (critical micellar concentration) is ~16 mM in this condition. The additional conditions that will be used to induce the necessary segments for multi-step self-assembly are (1) the addition of salt (potassium bromide) so that it can change the concentration of bromide ions and (2) the changes in the concentration of the building units. How these additional conditions change the attractive and repulsive forces, and thus induce the multi-step self-assembly, is discussed next.

Figure 4-2(b) shows the schematic illustration of the multi-step self-assembly of dodecyltrimethylammonium bromide. As pointed out in the previous chapter, this schematic illustration depicts the self-assembly process in a conceptual way. This should help guide us through the various concepts in understanding the self-assembly process. This is not actually what happens in a real self-assembly system. For the sake of simplicity, the detailed molecular structure is not included. The symbols for the attractive and repulsive segments are from Figure 1-3 and are exactly the same as those from the previous chapter.

Again, our understanding of the self-assembly process of any type of building unit has to begin with the attractive segment. At first, self-assembly building units have to be close together to eventually self-assemble. The attractive segment for dodecyltrimethylammonium bromide is the long hydrocarbon chain. Once they happen to be in the proximity whose range allows them to interact through hydrophobic force, they will begin to attract each other. If it is assumed, for the purpose of better schematic understanding, that there is no repulsive force that can counterbalance this attractive process, they will simply grow indefinitely until all of them are precipitated out. This is when the repulsive segment has to be brought into the picture. The repulsive segment of dodecyltrimethylammonium bromide is the electrostatic repulsive force. Once this force comes into play, it will counterbalance the attractive interaction, which will eventually lead the whole system to the point where the two opposite forces are balanced. This is the primary self-assembly of dodecyltrimethylammonium bromide. Thus, it should come as no surprise that the illustrative process is exactly the same as in Figure 3-2(b).

Now let us take a look at the conditional factors. They have a strong enough capability to change the segmental situation of dodecyltrimethylammonium bromide so that they can lead it to the next step of self-assembly. It might not be a strong enough argument to treat the self-assembled aggregate as the only major self-assembly building unit for the next step of self-assembly, especially in the sense that the whole self-assembly is a dynamic process and the self-assembled aggregate is always a dynamic object and not a static one. There are constant dynamic processes within the self-assembly system, such as exchange, assembly/disassembly, binding/dissociation, and so forth. However, as will be described in detail shortly, by approaching the next step of self-assembly as if it were another process of

self-assembly of the self-assembled aggregates that were formed from the previous self-assembly, the whole processes of multi-step self-assembly can be nicely included within the framework of the concept of segmental analysis. In this way, a rich conceptual understanding about self-assembly can be obtained, which can yield a wealth of useful applications. In fact, in most cases, the time scale difference between the dynamics of self-assembly building units and of self-assembled aggregates is orders of magnitude, which justifies this as a realistic case.

We now consider the self-assembly of the self-assembled aggregates (**P-SAA**). This is based on the assumption that conditional factors provide enough driving forces to the self-assembly system so this process can occur. The aggregate in this case is the micelle of dodecyltrimethylammonium bromide. Its size (diameter) can be assumed to be close to double the length of dodecyltrimethylammonium plus double the diameter of bromide ion. This makes the size roughly over 3 nm, which belongs to the length scale of colloidal particles. Its shape, with some possibility of distortion, can be assumed to be a spherical one. Thus, it will be a reasonable assumption that this aggregate that is formed from the primary self-assembly is a colloidal particle with a spherical morphology. Its surface is positively charged. This brings us back to Figure 3-5(a) for its segmental analysis. Figure 3-5(a) was for silica colloidal particle, which was solid with a very limited possibility of exchange dynamics of its component. However, it was established that self-assembled aggregates can be considered as an analogue of colloidal particles as far as the segmental analysis is concerned. There will be van der Waals force between the aggregates since the time scale of assembly–disassembly of the aggregates should be much slower than the time scale of van der Waals force interaction. And the main component of dodecyltrimethylammonium bromide is an ordinary hydrocarbon chain. This means, as with silica particle, that van der Waals interaction becomes an attractive segment of the aggregate. For the repulsive segment, attention should be on negatively charged nitrogen atoms. For silica particle, it was the surface charges that were permanently attached on its surface. There was an exchange of surface charge groups with the solution, but its dynamic was minimal. For the nitrogen atoms, they are not permanently attached on the surface of the aggregates. They are constantly exchanged with the solution as dodecyltrimethylammonium molecules are being exchanged with the solution. In addition, the bromide anions are constantly bound on the surface of the aggregate and released from it. However, the time scales for all these dynamics are much slower than the time scale of the interaction induced by the negatively charged nitrogen atoms on the surface of the aggregate. Therefore, it will be safe to conclude that the electrostatic interaction that is generated by this surface charge is the repulsive segment of the aggregate. As conditional factors allow the force balance between these two segments, the aggregates will self-assemble. The aggregates are now the self-assembly building unit. Thus, they are the secondary self-assembly building unit, and the process is the secondary self-assembly. Dodecyltrimethylammonium molecules were the building unit for the primary self-assembly.

The schematic understanding of the secondary self-assembly also begins with an attractive segment. There is an attractive segment within the secondary

self-assembly building units; therefore, when they happen to be close enough, they will attract each other through the attractive force. If there is no repulsive segment, the aggregates will grow indefinitely. However, the repulsive electrostatic force will come into play and counterbalance the attractive force until they are balanced. Notice that this schematic illustration is exactly the same as Figure 3-5(b), which again should come as no surprise. The self-assembled aggregates formed as a result of this process are the secondary self-assembled aggregates. If conditional or any structural factors allow them to continue the assembly process, they can be called the tertiary self-assembly building unit and their assembly process is the tertiary self-assembly.

Four different self-assembly conditions are shown in Figure 4-3. The self-assembly building unit is dodecyltrimethylammonium bromide for all cases. Let us consider the general tendency of their self-assembly from the system at the left-hand side to the one at the right-hand side. For all of them, it is assumed that the condition is in water at room temperature. It begins with 25 mM of dodecyltrimethylammonium bromide. It is well documented that dodecyltrimethylammonium bromide self-assembles at this condition with the *cmc* of ~16 mM. A typical cationic micelle with spherical shape is formed at this concentration and stays as stable solution. This means that it does not go into the next step of self-assembly. The next system has the same building unit at the same concentration of 25 mM but with 25 mM of potassium bromide. The potassium bromide provides excess amounts of bromide anions. By combining with the bromide anions that come from the building unit, the solution now has more counterions that have the capability of being attached

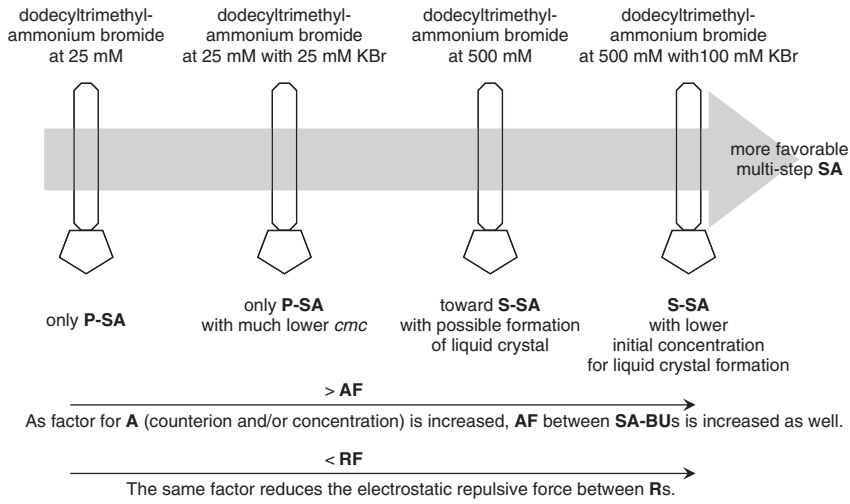


Figure 4-3. Self-assembly of dodecyl trimethyl ammonium bromide in water at room temperature with different conditions of salt and concentration. **A** and **R** refer to attractive and repulsive segments, respectively. **AF** and **RF** refer to attractive and repulsive forces, respectively. **SA, P-SA**, and **S-SA** are short for self-assembly, primary self-assembly, and secondary self-assembly, respectively. **SA-BU** is self-assembly building unit. *cmc* is critical micellar concentration.

to the surface of the aggregates (micelles). A simple equilibrium consideration suggests that this excess amount of bromide anions will push their equilibrium with the negatively charged surfaces toward more bromide anions to be bound on the surface of the micelles. This happens through electrostatic interaction. As far as the segmental analysis is concerned, this is simply the decreasing of the repulsive force between the micelles. The decreased surface charge (decreased density of negatively charged nitrogen atoms) should mean the decreasing of the electrostatic repulsive force. The nature of the repulsive segment is the same, but its degree is now decreased. On the other hand, the attractive segment, which is a dodecyl hydrocarbon chain, should remain nearly the same. This type of variation in the segmental structure is a typical one that should make the self-assembly more favorable compared with the one without the excess counterions. The result is evidenced by a lower value of *cmc*. But the concentration is still not high enough to push this self-assembly system to the next step of self-assembly, which is backed by experimental reports. The self-assembly is still a primary one with the same type of aggregates.

The third self-assembly system is the one with the same building unit but at a much higher concentration of 500 mM. It has no added salt. By increasing the concentration of the building units 20-fold, it can be assumed that the concentration of the aggregates is also increased. This will not change the degree of electrostatic interaction between the aggregates since the degree of counterion binding would be nearly the same. However, the increased concentration of the aggregates not only increases the frequency of the direct interactions between them but increases the possibility of the fusion type of interactions as well. With the fact that the size of the aggregates is increased to a somewhat significant degree, this causes the increasing of the attractive force between them. Thus, in the segmental structure compared with the second system the repulsive segment remains nearly the same while the attractive segment is increased.

The segmental structure of the aggregates now favors their self-assembly. This is evidenced by numerous literature reports. It is thus safe to conclude that this system continues to assemble into the secondary self-assembly after the formation of the primary aggregates. New aggregates formed by the self-assembly of the primary aggregates should be in a stacked (or packed) form or a form distorted (or evolved) from the primary aggregates. Typically, this is a liquid crystal. The last self-assembly system has the same concentration of 500 mM of dodecyltrimethylammonium bromide as for the third system but with 100 mM of potassium bromide. The same segmental analysis can be performed as was done in comparing the second system with the first one. An important difference again is that, for this comparison, it is the segments of the primary aggregates that are analyzed. The increased amount of counterions (compared with the third system) acts to decrease the repulsive segment of the primary aggregates through the increased degree of counterion binding on the surface of the primary aggregates. The attractive segment should remain nearly the same based on the reasonable assumption that there is no significant change in the structures and sizes of the primary aggregates. Once again, this is a typical case for the change in segmental structures, which should

promote more favorable self-assembly that continues into the secondary self-assembly. Typically, this secondary self-assembly also yields liquid crystals. But the concentration where the initial formation of the liquid crystal occurs should be much lower. This is also well proved by the literature results.

The general trend of multi-step self-assembly of this particular group of self-assembly systems can now be established. As it goes in the direction of increasing the concentration of self-assembly building units and/or the addition of salts that produce the same kind of counterions, the possibility of multi-step self-assembly is increased in a more favorable way. The attractive force between the building units or between the primary aggregates is increased. At the same time, the repulsive force is decreased because of the decreased electrostatic repulsion. This general trend works not only for this particular group of cationic surfactant systems but for most other molecular building units as well. It includes amphiphilic polymers, bio-mimetic molecules, and biologically originated molecules. As long as their molecular structures are clearly identified so that the proper segmental analysis can be performed, and as long as the sizes of their self-assembled aggregates are within the length scale of colloids, their multi-step self-assembly processes should follow the schematic illustration drawn here. With a proper reference system, their self-assembly parameters can be predicted as well, at least qualitatively. It is possible even semiquantitatively in many cases. In addition, it can work for self-assembly systems with different types of added counterions and with different types of cosolvents.

Case Study 4.1

Simulation studies for the normal and reverse bilayers of amphiphilic surfactants were performed with a very similar concept of the force balance between the attractive and repulsive segments (Stecki, 2008). The hydrophobic effect between the hydrocarbon chains was the attractive force while the interactions between the head groups were adopted as the repulsive force. In addition, both the attractive and repulsive forces were varied in a systematic manner for the assembly of the reverse bilayers of amphiphilic dimers. The results that showed the critical changes in the lateral tension at a certain value of area-per–head group well comport with the discussion made in this subsection.

4.3.2. Colloidal Self-Assembly

Among different colloidal particles, silica may be the most typical and widely used one. It thus brings so much practical usefulness to the understanding of the self-assembly of colloidal particles. Figure 4-4 shows the self-assembly of silica colloidal particles. The experimental condition is in water at room temperature at high solution pH. The conditions to induce multi-step self-assembly are the addition of salt and depletion agent. Once again, we consider the self-assembly tendency from the left-hand side to the right-hand side. Parallel comparison with the examples in Figure 3-7 will provide a better understanding of this group. The segmental analysis of the silica particle is the same as in Figure 3-5(a).

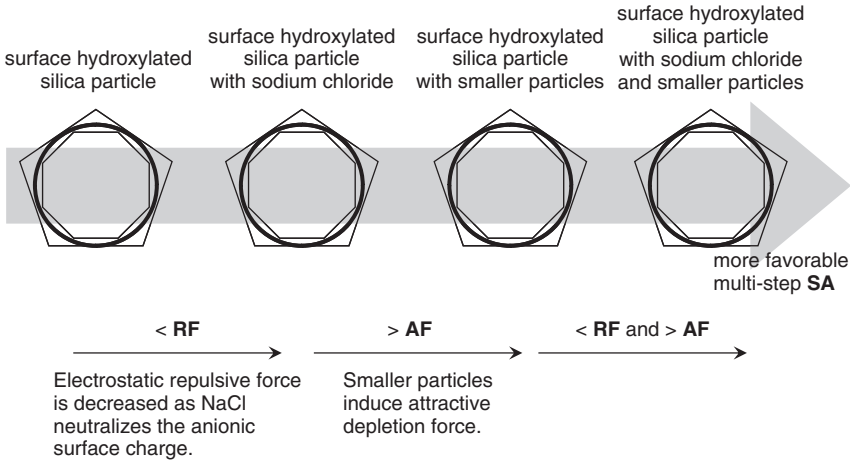

surface hydroxylated silica particle
surface hydroxylated silica particle with sodium chloride
surface hydroxylated silica particle with smaller particles
surface hydroxylated silica particle with sodium chloride and smaller particles
more favorable multi-step SA
< RF
> AF
< RF and > AF
Electrostatic repulsive force is decreased as NaCl neutralizes the anionic surface charge.
Smaller particles induce attractive depletion force.

Figure 4-4. Self-assembly of silica colloidal particles in water at room temperature at high pH with different conditions of salt and depletion agent. **AF** and **RF** refer to attractive and repulsive forces, respectively. **SA** is self-assembly.

The one on the far left-hand side is the silica colloidal particle with its surface hydroxylated. The high solution pH gives the ideal condition to have this surface deprotonated, which means that the silica surface is covered with negatively charged oxygen atoms. As shown in Figure 3-7, the balance between the attractive van der Waals force and the repulsive electrostatic force makes this silica particle self-assemble as long as the solution condition is set properly. Let us assume that we have the silica particles at this proper solution condition. The next system of silica particle is the same as this but with an added salt. Sodium chloride is introduced. Once in the solution, it will decrease the charge density on the silica surface significantly through its binding on the deprotonated surface hydroxyl groups.

As for the segmental structure, this means the decreasing of the repulsive force. The attractive van der Waals force can be assumed to remain nearly the same since there is no major change in any of its components. This type of change in segmental structure is favorable for self-assembly. For the third system, it is chosen such that the same silica particle whose surface is hydroxylated is now with another particle having much smaller size. The smaller particle is assumed to have no significant electrostatic interaction with the silica particle. Its role is to induce the depletion force that is generated when smaller particles are located between bigger particles. This induces the attractive force between the silica particles. The charge density on the surface of the silica particle is still the same, but now there is an additional force (depletion force) that is attractive. The term *depletion agent* derives from this fact. Hence, the segmental structure for this third system compared with the second one is such that it has the same repulsive force but with increased attractive force.

This, of course, is one of the ideal changes in segmental structures for more favorable self-assembly. Since the conditions for the salt and charge density are not specific for this particular system, it would not be certain that this would be enough

to induce this system to go into multi-step self-assembly. A simple experiment can confirm that. Should there indeed be multi-step self-assembly, its secondary self-assembled aggregates would have a higher possibility of showing a fractal nature of morphology rather than the compact nature of the primary aggregates unless the attractive force is overwhelmingly higher than the repulsive force. This could serve as a good focal point when the actual experiment is performed.

Let us assume that the third self-assembly system indeed has the capability of multi-step self-assembly. And let us consider the fourth system. It is again the silica particle with its surface hydroxylated, but now it is with sodium chloride, the amount of which is the same as for the second system, and with the smaller particles that are the same as for the third system. Compared with the third system, this system has less repulsive force because of the sodium chloride. Compared with the second system, this system has more attractive force because of the depletion agent. This segmental structure gives the fourth system the most favorable self-assembly conditions among the four systems, which makes it the most favorable for multi-step self-assembly. Generally speaking, as we go from the system on the left-hand side to the one on the right-hand side, the attractive force is increased by the experimental conditions, and at the same time the repulsive force is decreased also by the experimental conditions. It is in this direction that the silica particles will self-assemble in more favorable way.

The understanding of the self-assembly of colloidal particles based on the segmental analysis and the general trend established from it can be expanded for many different types of colloidal self-assembly systems. This includes polymeric particles, metal oxide particles, pure metallic particles, and even biological particles. A careful analysis of the segmental structure of their building units is the most important step. If there are new factors, whether they are intrinsic or conditional, possible new segments should be identified and assigned. For example, if a colloidal particle with nonspherical shape (such as rod or tube) is under consideration, a new attractive segment is likely induced by the capillary force. Then, it should be included into the overall segmental structure.

Case Study 4.2

A simulation study (Miller and Cacciuto, 2009) that shows the self-assembly of asymmetric amphiphatic colloidal particles nicely backs up the general trend established in this subsection. As they increase the ratio of the hydrophobic region (attractive segment) to the hydrophilic region (repulsive segment), the morphologies of the self-assembled aggregates of the colloidal particles vary from the small micellar-like clusters to much larger aggregates. The results further provide clear evidence of hierarchical (multi-step) self-assembly processes, and both the aggregation numbers and sizes of the aggregates are apparently increased. At the highest ratio of the hydrophobic region to the hydrophilic region, aggregates with fcc crystal order were formed. Furthermore, their discussions on the stepwise self-assemblies based on the notion of force balance are comparable to the concept of segmental analysis. So is the result that shows

that even a small perturbation of the segmental structure can lead to significant changes in the morphologies of self-assembled aggregates through force rebalance.

Case Study 4.3

There is an excellent experimental observation (Bonn et al., 2009) that shows the formation of fractal clusters from fluorinated latex colloidal particles in the binary solvent of water-3-methylpyridine. What is special for this system is that, through a refractive index matching between the colloid and binary solvent, the van der Waals force, which is one of the most common attractive segments for colloidal self-assembly, becomes negligible. Instead, the critical Casimir force is induced. This force is attractive, and thus becomes the attractive segment of the latex particle. The Coulomb force is its repulsive segment. The self-assembled aggregates of the particles are formed through the balance between these two opposite forces. This interesting self-assembly is reversible, and the aggregates are observed in a wide range of temperature. The microscope images that show the growth of the clusters into network morphologies strongly suggest that the hierarchical self-assembly takes place in this colloidal system.

4.4. COLLECTION OF HIGHER-ORDER SELF-ASSEMBLED AGGREGATES

Table 4-1 lists the collection of self-assembled aggregates. They are higher-order self-assembled aggregates, which means that they are the aggregates that appear after the formation of the primary self-assembled aggregates. The collection of primary self-assembled aggregates was listed in Table 3-1. Most of them are secondary self-assembled aggregates; in the other words, they are the aggregates formed during the secondary self-assembly. Thus, their lower-order self-assembled aggregates are mostly those primary self-assembled aggregates shown in Table 3-1. Like the primary aggregates, some of the higher-order aggregates that usually appear in solutions can be formed at the surface, too. But those that are referred to a result of surface multi-step self-assembly are almost solely formed at surfaces.

As with those in Table 3-1, the names of each of the higher-order aggregates are those that frequently appear in the literature. Often, some discrepancies are found among different journals even though they describe the same or very similar systems. The description for each aggregate in the table along with those for the lower-order aggregates in Table 3-1 should be helpful for clarification. Otherwise, whenever one of these names is used, it is almost certainly a higher-order self-assembled aggregate. Once the identity and origin of each aggregate becomes clear, the understanding of its dynamics and physical properties can be more systematic. Table 4-1 also gives the segment combination and kind of building units with which each aggregate is most likely obtained. Compared with the primary aggregates, the segment combination becomes a little more complicated, and the kind of building units for some higher-order aggregates becomes less diverse. This should come as

TABLE 4-1. Collection of higher-order self-assembled aggregates, a brief description of each of them, their lower-order aggregates, and the segment combination and kind of building units with which each self-assembled aggregate is most likely formed through hierarchical self-assembly. m, c, p, b, b-m indicate molecular, colloidal, polymeric, biological, and bio-mimetic building units, respectively. A, R, R^c, D, and AP refer to attractive, repulsive, conditional repulsive, directional, and asymmetric packing segments, respectively. seg. com., surf., l.c., and poly. are short for segment combination, surfactant, liquid crystal, and polyelectrolyte, respectively. SAA is self-assembled aggregate.

Name	Description	Building Unit		
		Lower-Order **SAA**	Seg. Com.	Kind
mesophase	surf. l.c.	surf. micelle	any one with **A** and **R**	m, p, b, b-m
reverse mesophase	reversed surf. l.c.	reversed surf. micelle	any one with **A** and **R**	m, p, b, b-m
gel	entangled fibrous **SAA** in solution	fibrous micelle	any one with **D** and **AP**	m, p, b, b-m
fiber	elongated threadlike aggregate	fibrous micelle	any one with **D** and **AP**	p, b, b-m
J-aggregate	assembled with end-to-end mode	dimer, multimer	dye with **A, R**, and **D**	m
vesosome	large unilamellar vesicle with smaller vesicles inside	vesicle	lipids with **A** and **R**	b, b-m
hexosome	bicontinuous emulsion with internal hexagonal phase	vesicle, micelle	lipids with **A** and **R**	b, b-m
cubosome	bicontinuous emulsion with internal cubic phase	vesicle, micelle	lipids with **A** and **R**	b, b-m
H-aggregate	assembled with face-to-face mode	dimer, multimer	dye with **A, R**, and **D**	m
Langmuir-Blodgett (LB) multilayered film[a]	multilayered LB monolayer	LB monolayer	any one with **A** and **R**	m, c, p, b, b-m
layer-by-layered film[a]	multilayered poly. film	poly. monolayer	poly. with **A** and **R**	p
sol-gel processed film[a]	multilayered film formed via sol-gel process	precursor coated-**SAA**	any one with **A** and **R** (or **R**^{c})	m
vapor-deposited multilayer[a]	multilayered film deposited by vapor deposition	deposited monolayer	any one with **A**	m, b, b-m
colloidal crystal	ordered 3D colloidal particles	colloidal cluster	any one with **A** and **R**	c
collagen fiber	threadlike aggregate	collagen triple-helix	with **A, R, D**, and **AP**	b
cellulose fiber	threadlike aggregate	cellulose thread	with **A, R, D**, and **AP**	b

[a]Self-assembled aggregates formed as a result of surface multi-step self-assembly. All the others are formed via multi-step self-assembly in solutions.

no surprise because for higher-order aggregates there should be always a strong enough driving force to bring the building units at least up to the secondary self-assembly.

There is also an important difference compared with the primary aggregates. For those primary aggregates, the segment combination was usually an absolute condition. Whenever the structural condition for the building units was properly met, it was almost certain that there would be self-assembled aggregates. But for those higher-order aggregates, the segment combination is often a necessary condition. In addition to the proper structural condition for the building units, experimental conditions have to be considered to obtain a necessary driving force. The experimental conditions that are frequently used are concentration, counterions, cosolvents, solution pH, and other additives. Some of the repulsive segments in the table are conditional. For more about its definition and function, please see Subsection 1.5.1.

The issue of why a certain form of higher-order aggregate is most likely obtained for a certain type of building unit is not as straightforward as for the primary aggregates. This is especially true when a certain experimental condition becomes a main factor. However, by cross-examining against the building units in Section 1-5 and the primary aggregates in Table 3-1, this can be usually addressed with a reasonable reliability. This in turn can help in designing nanotechnology systems having more complicated structures and functions. For example, we saw in Section 3.4 that, by reasonably predicting which building unit can give what type and size of micelles, the design of the sizes and properties of nanoscale morphologies can be more practical. Now, by reasonably predicting which building unit can give what type and size of mesophase (whose primary aggregates are micelles), the design of the overall arrangement and hierarchy of those nanoscale morphologies can be more systematic. For another example, by predicting which type of building unit gives the aggregates with fibrous structure and which one gives the aggregates with linear structure, the design of nanotechnology systems that require helical functionality or straight channel can be better planned rather than mere random trials. As shown in Table 4-1, the key thing to look for is whether the building unit has an asymmetric packing segment. Whenever this segment is identified within the building units, it is fairly certain that the aggregates show a fibrous structure with a certain helicity.

4.5. COLLECTION OF SELF-ASSEMBLED AGGREGATES WITHIN BIOLOGICAL SYSTEMS

Biological systems have a variety of self-assembly processes and a full of self-assembled aggregates. Many physical and chemical processes that are vital for their reproduction and survival are closely related to those self-assembly processes. Also, many of the physical and chemical functionalities of the biological systems rely on the functionalities, rigidity, and at the same time flexibility of those self-assembled aggregates. Some of them are relatively simple primary aggregates. But the majority of them are higher-order aggregates. Many of them are actually

reaching hierarchies way beyond the secondary self-assembly. Tertiary and even higher-order aggregates are not uncommon within biological systems.

Table 4-2 lists the collection of the self-assembled aggregates that are found within biological systems. These are the most common ones, and it is certainly not a full list. This table reiterates the following important observations regarding biological self-assembly:

1. The assembly of these biological aggregates can be understood by carefully analyzing the structures of their building units (segmental analysis), the same as for nonbiological aggregates.
2. Their structures are so elegant and functional that they fit remarkably well with the environmental conditions they are in.
3. Thus, they yield rich implications and great usefulness for designing nanotechnology systems.

More examples and discussions of these important issues are found in Figures 7-5, 12-6, 14-5, 14-9, and 14-10. Table 14.1 has many examples, too. As indicated in Table 4-2, for most of the biological aggregates, it is not that difficult to find a resemblant nonbiological system. The assembly processes, morphologies, and functionalities of the biological aggregates are strikingly similar with these resemblant systems, which is a key reason that they are often used as model systems for the biological aggregates. Model systems allow us to study the related parameters in a systematic manner, otherwise it would be quite challenging, especially *in vivo*. The lower-order aggregates of the biological aggregates can also be easily indentified. By acknowledging these factors, applying biological aggregates for nanotechnology systems becomes more practical.

4.6. SUMMARY

This chapter addressed the second key question for the self-assembly systems that can be pursued once it is confirmed that their building units have indeed the capability of self-assembly. The question was whether the building units have the capability to continue into multi-step self-assembly. This chapter showed that this second question can be answered almost exactly the same way as we answered the first group of questions in Chapter 3. More precisely:

1. The structural analysis of the primary self-assembled aggregates provides useful means to understand their self-assembly.
2. If this segmental analysis shows favorability of self-assembly, they have the capability to form higher-order aggregates.
3. With a proper reference system, this approach can allow us to predict the second critical assembly parameters [the second *cmc* (critical micellar concentration) and the second *can* (critical aggregation number)] in a systematic manner.

TABLE 4-2. Collection of self-assembled aggregates within biological systems, a brief interpretation of their assembled states, their lower-order (basic) assembled aggregates, and their resemblant assembled aggregate outside biological systems. SAA is self-assembled aggregate.

Name	Description	Lower-Order (Basic) **SAA**	Resemblant Nonbiological System
plasma membranes	lipid bilayers assembled with other components	bilayer	vesicle
mitochondrial membranes	lipid bilayers assembled with other components	bilayer	vesicle
nuclear envelops	lipid bilayers assembled with other components	bilayer	vesicle
proteins	chains of amino acids that are coiled/folded/assembled	amino acid chain	polymer aggregate
enzymes	proteins having catalytic activity	amino acid chain	polymer aggregate
ribosomes	assembled rRNA-protein complex	ribosomal subunit	hetero-(or mixed) polymer aggregate
microtubules	assembled tubulin subunits	α,β-tubulin dimer	tubular micelle
actin bundles	assembled actin filaments with proteins	actin filament	side-by-side rod aggregate
lysosomes	vesicle contains enzymes	bilayer	vesicle
vacuoles	vesicle bound by single membrane	bilayer	vesicle
peroxisomes	small vesicle bound by membrane	bilayer	vesicle
ensosomes	vesicle formed during endocytosis	bilayer	vesicle
mesosome	vesicular form in plasma membrane of bacteria	bilayer	vesicle
viruses	assembled nucleic acid-protein complex	protein subunit	mixed micellar rod or tube
collagen fiber	hierarchically assembled collagen α-helix	collagen helix	polyelectrolyte aggregate rod
DNA double helix	two antiparallel chains of complementary polynucleotides	DNA chain	polymer inter-aggregate
RNA chains	right-handed stacking of single RNA strand	RNA chain	polymer intra-aggregate
cells	all systems above assembled functionally	all **SAA**s above	vesosome

Finally, it is worth remembering that, for multi-step self-assembly, the possibility of more complicated dynamics of the higher-order building units than those of primary building units and the polydispersity of the higher-order aggregates can often become difficult issues for a proper structural analysis.

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5

Control of the Structures of Self-Assembled Aggregates

5.1. ASSEMBLY ISSUE

The previous two chapters addressed two key questions regarding self-assembly systems. They showed that both of the questions can be answered in a systematic manner with the structural analysis of assembly building units (*segmental analysis*—see Subsection 1.2.2 for its details). They also indicated that the self-assembled aggregates that were formed in each step of self-assembly were subject to dynamic structural changes. This naturally leads us to the next important question that is necessary for a full understanding of self-assembly systems. It is in regard to what the self-assembled aggregates at each step of self-assembly will look like and behave like. Thus, the question we will be asking in this chapter goes as follows:

What will be the most probable structure of your self-assembled aggregates?

We also have learned from the previous two chapters that the primary self-assembled aggregates are formed through the primary self-assembly of molecules or colloidal particles. In other words, their self-assembly building units are individual objects. But for the higher-order self-assembled aggregates, which include secondary aggregates, tertiary aggregates, and more, their main self-assembly building units are the self-assembled aggregates that are formed from the previous step

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of self-assembly. They are not individual objects. Rather, they are aggregates that are always dynamic. More precisely, this assumption was necessary so that the concept of segmental analysis could be expanded for those dynamic building units. This leads us to break the question of this chapter into two parts:

What will be the most probable structure of your primary self-assembled aggregates?

What will be the most probable structure of your higher-order self-assembled aggregates?

This chapter shows how to address the structures of the primary aggregates by using the segmental analysis. It also shows that the same goes for the higher-order aggregates: segmental analysis of each building unit and the subsequent consideration of the concept of force balance. However, there is an important difference. The wide structural varieties of the aggregates at each step of self-assembly in many cases come from the strong yet intricate involvement of two other segments in addition to attractive and repulsive segments. These are the directional and asymmetric packing segments. Many details regarding the role of these two segments will be discussed throughout this chapter.

5.2. GENERAL OVERVIEW

5.2.1. Primary Self-Assembled Aggregates

Figure 5-1 shows a general overview of the identification of the structures of the primary self-assembled aggregates. A directional force that is induced by a directional segment is heavily involved. A directional segment is a segment that generates some degree of the directionality of self-assembly. Another factor that is important for the discussion in this section is the asymmetric packing segment. This segment generates diverse and sometimes very tricky changes in the packing mode of a given building unit.

Let us begin with the building unit that is a molecule or colloidal particle and is proven to have the capability of self-assembly. The first question to ask is whether this building unit has an asymmetric packing segment. If the answer to this question is no, then the primary aggregate will most likely have a symmetric morphology. This is because, in most cases, it is the asymmetric packing segment that causes the asymmetric morphology due to its tendency to pack the building units asymmetrically. The next issue is the directional segment. The question is whether the building unit has a directional segment or whether there is any external factor that can provide a directional force to the self-assembly system. If the answer to this question is no, the building unit has only the attractive and repulsive segments. Therefore, the primary aggregate will be likely a nonlinear or globular structure with three-dimensional symmetry. This will be called *example I* for the later discussion. If the answer is yes, the primary aggregate will be likely linear or circular because of the impact of the directional segment. The structure will likely have two-dimensional symmetry. This will be called *example II*.

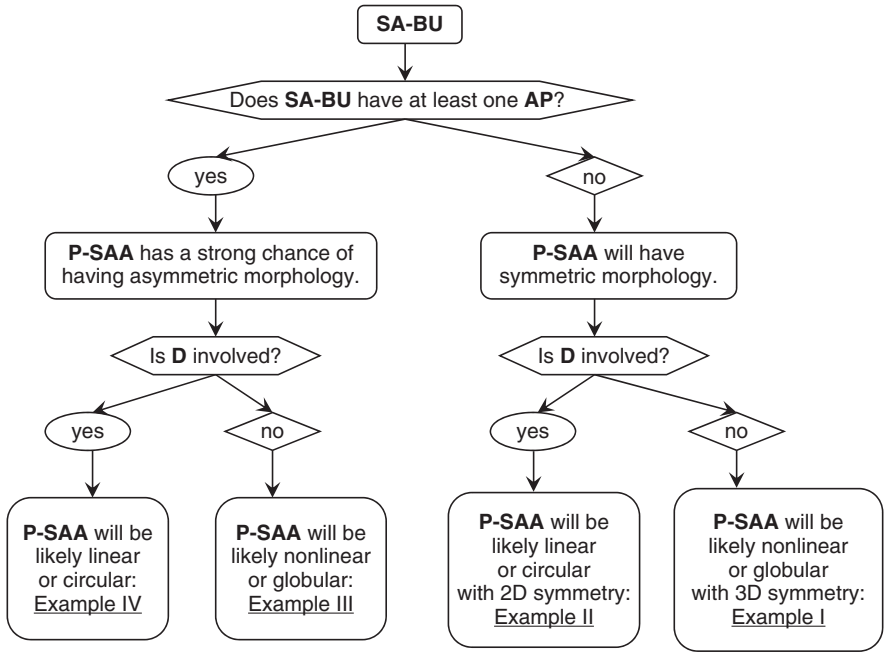

SA-BU
Does SA-BU have at least one AP?
yes
no
P-SAA has a strong chance of having asymmetric morphology.
P-SAA will have symmetric morphology.
Is D involved?
Is D involved?
yes
no
yes
no
P-SAA will be likely linear or circular: Example IV
P-SAA will be likely nonlinear or globular: Example III
P-SAA will be likely linear or circular with 2D symmetry: Example II
P-SAA will be likely nonlinear or globular with 3D symmetry: Example I

Figure 5-1. General overview of the identification of the structure of the primary self-assembled aggregate (**P-SAA**) of a given self-assembly building unit (**SA-BU**). **D** and **AP** refer to directional and asymmetric packing segments, respectively.

On the other side of the flowchart, if the answer to the first question is yes, the primary aggregate has a strong chance of having an asymmetric morphology. It will be almost exclusively the result of the action of the asymmetric packing segment. The next question is whether any directional segment or factor is involved in the self-assembly process. If the answer to this question is no, the primary aggregate will more likely have nonlinear or globular structure. An asymmetric packing segment without the aid of a directional segment can sometimes induce the symmetric globular morphology. This is *example III*. The final case is when the answer is yes. This is when the given building unit has both the asymmetric packing and directional segments in addition to the attractive and repulsive segments. The possibility of the primary aggregate having a symmetric morphology will be almost negligible unless the effects of the asymmetric packing segment and of the directional segment work in completely opposite directions so that they can counterbalance each other. The primary aggregate will be most likely linear or circular. This will be called *example IV*.

5.2.2. Higher-Order Self-Assembled Aggregates

Figure 5-2 shows a general overview of the identification of the structures of higher-order self-assembled aggregates. Higher-order aggregates here means all of the

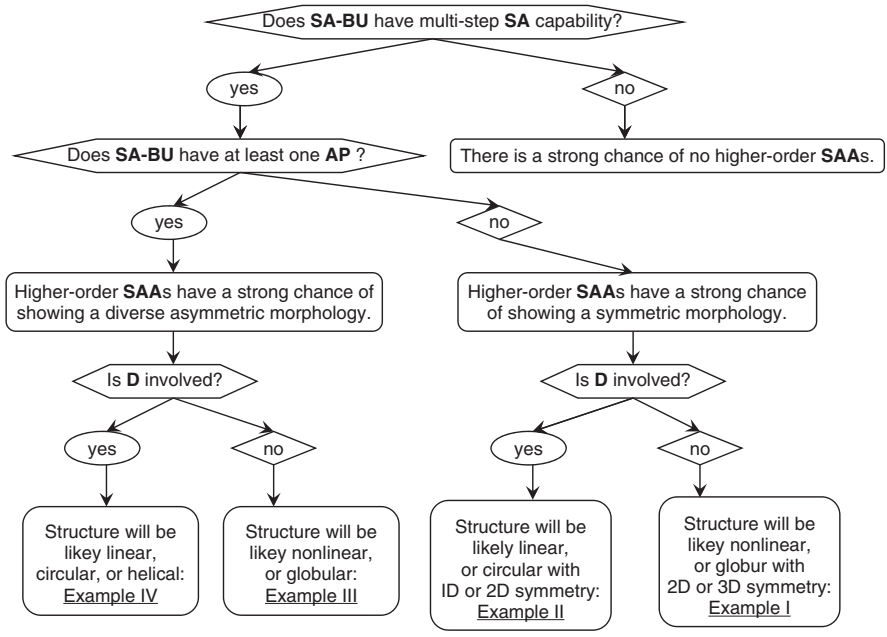

Does SA-BU have multi-step SA capability?
yes
no
Does SA-BU have at least one AP ?
There is a strong chance of no higher-order SAAs.
yes
no
Higher-order SAAs have a strong chance of showing a diverse asymmetric morphology.
Higher-order SAAs have a strong chance of showing a symmetric morphology.
Is D involved?
Is D involved?
yes
no
yes
no
Structure will be likey linear, circular, or helical: Example IV
Structure will be likey nonlinear, or globular: Example III
Structure will be likely linear, or circular with ID or 2D symmetry: Example II
Structure will be likey nonlinear, or globur with 2D or 3D symmetry: Example I

Figure 5-2. General overview of the identification of the structure of the higher-order self-assembled aggregate of a given self-assembly building unit (**SA-BU**). **D** and **AP** refer to directional and asymmetric packing segments, respectively. **SA** and **SAA** are short for self-assembly and self-assembled aggregate, respectively.

self-assembled aggregates that are formed after the primary self-assembly—in other words, all of the aggregates formed from the secondary self-assembly, tertiary self-assembly, and so on. The fundamental differences between the primary aggregates and the higher-order aggregates come from the integrity of their building units. For the former, it is an individual molecule or colloidal particle, but for the latter, it is the self-assembled aggregate that is formed in the previous step of self-assembly. Figure 5-2, in this sense, could have been drawn in a more complicated way to include the dynamic nature of the aggregates. Instead, this figure is designed through a simple combination of Figure 5-1 (which was to determine the structure of the primary aggregates) with Figure 4-1 (which was to figure out the capability of multi-step self-assembly). It will be shown later that this rather simplified flowchart works better when it comes to predicting the best possible structures of the higher-order aggregates.

The first question to ask is whether a given building unit has the capability of multi-step self-assembly. For this question it is assumed that the building unit is proven to have the capability of primary self-assembly. If the answer is no, it is highly likely that there is no possibility of forming higher-order aggregates. If the answer, however, is yes, it is almost certain that there will be higher-order aggregates, and the next question should be asked. This is whether the building unit has at least one asymmetric packing segment. The dynamic nature of the

higher-order aggregates and the relevance of the segmental analysis for them were discussed in the previous chapter, which suggests that the rest of the flowchart for the involvement of the directional segment can be the same as the one in Figure 5-1. A key difference is that the object of interest is now the higher-order aggregates instead of the primary aggregates. The numbering with capital letters for each example parallels that in Figure 5-1.

5.3. ASSEMBLY PRINCIPLES

5.3.1. Primary Self-Assembled Aggregates

Figure 5-3 is a schematic explanation of the structure identification of the primary self-assembled aggregates. It shows how segmental analysis can help determine the structure of each example in Figure 5-1. The numbering with capital letters parallels that in Figure 5-1. The symbols representing each segment are from Figures 1-3 and 1-5. For the sake of simplicity, these schemes are drawn for molecular building units. But they work well for colloidal building units as well.

Example I in Figure 5-1 is for the building unit with an attractive segment and a repulsive segment. As discussed in the previous two chapters, the force balance

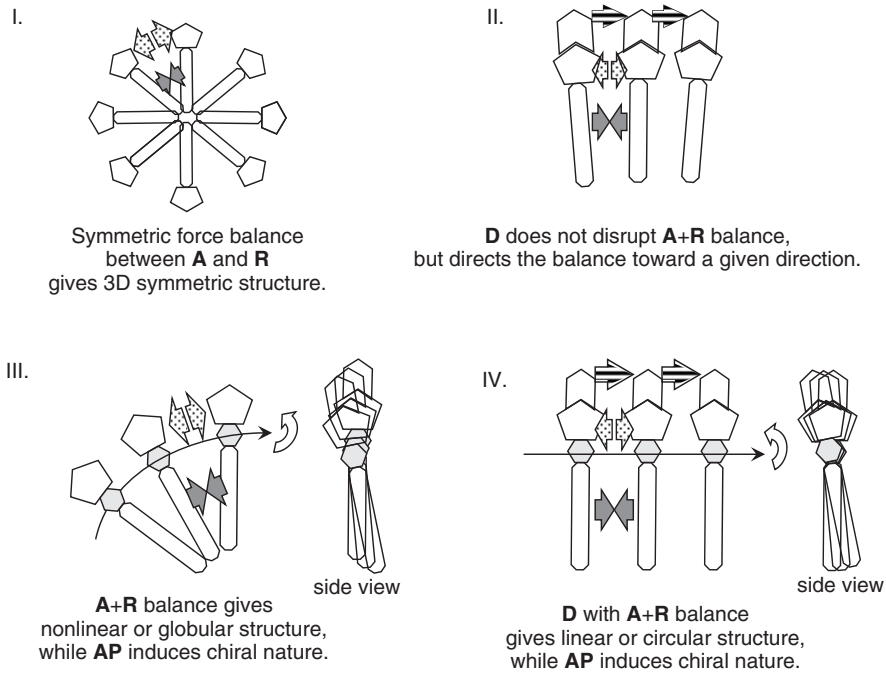


Figure 5-3. Schematic explanation of the structure identification of the primary self-assembled aggregate of a given self-assembled building unit. **A, R, D**, and **AP** refer to attractive, repulsive, directional, and asymmetric packing segments, respectively.

between these two segments is symmetric. There may be some local fluctuation since the primary aggregates are always a dynamic object. But this notion of symmetric force balance stands valid because the purpose of this chapter is to identify the overall morphology of the primary aggregates as if they were static. In other words, the morphology determination has to be performed with a time scale much slower than the time scale of their dynamics. This will give the primary aggregates a high possibility of three-dimensional symmetric overall structure unless this symmetric force balance is significantly perturbed, for example, by the interaction with surfaces (surface self-assembly). As shown in Figure 5-1, the terms *nonlinear* or *globular* will be useful to represent this structure. *Nonlinear* here does not mean every possible structure that is not linear. It should be interpreted that the structure is more likely spherical or a slightly derived shape such as ellipsoidal. Example II in Figure 5-1 becomes the self-assembly system whose segmental structure consists of an attractive segment and a repulsive segment combined with a directional segment. Once its primary self-assembly produces the primary aggregate, there is no reason that the balance between the attractive and repulsive segments is disrupted by the presence of the directional segment. What the directional segment does is to direct the primary self-assembly process. In many cases, the directional segment can also act as a second attractive or repulsive segment, thus reinforcing either the attractive or repulsive force. This condition gives the primary aggregates a high chance of being a linear type of morphology. *Linear* here does not necessarily mean a long wirelike one-dimensional structure. It is rather close to the round-shaped globular structure with its overall shape somewhat (or significantly, depending on the strength of the directional force) distorted. For many self-assembly systems of this type, the primary aggregates often have a segmental structure that can make a full circle of distortion, which ends up forming a circular type of overall morphology.

For example III in Figure 5-1, the role of the asymmetric packing segment becomes critical for the overall morphology of the primary aggregates. For convenience, the asymmetric packing segment, which is represented with a gray-filled hexagon, is located between the attractive and repulsive segments. But, in actual systems, this segment, like any others, can be located at any position. The additional scheme on the right-hand side is to show the side view of a part of the primary aggregate where the effect of the asymmetric packing segment is prominent. Since this example does not have a directional segment, the balance between the attractive and repulsive segments will yield a nonlinear or globular type of overall morphology, just like the first example. But it is the role of the asymmetric packing segment to have the building units packed as if they were not symmetrically eclipsed by each other. The side view shows better what this means. It thus can create more varieties of structural possibilities compared with example I, but still with the nonlinear or globular overall shape. This often induces a chiral nature of morphology, too.

Example IV in Figure 5-1 has all four segments: attractive, repulsive, directional, and asymmetric packing segments. As in example III, the side view shows the effect of the asymmetric packing segment. As in example II, the combination of the attractive and repulsive segments with a directional segment yields a high

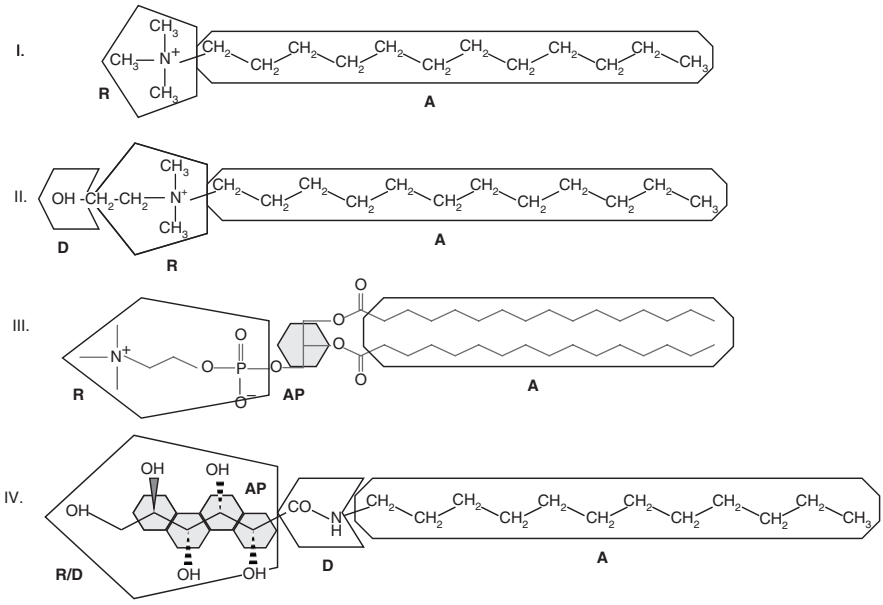
possibility of linear or circular morphology for its primary aggregate. And it is again the effect of the asymmetric packing segment that can make this example such a morphologically rich system including a chiral nature.

5.3.1.1. Molecular Systems I. Figure 5-4 illustrates examples of the structure determination of primary self-assembled aggregates. Four self-assembly building units are shown. The first two are molecular building units and the other two are biologically derived building units. All of them are well-known for forming self-assembled aggregates through well-defined self-assembly processes under the condition given here. The condition is assumed to be in water at room temperature. The numbering with capital letters parallels that in Figures 5-1 and 5-2.

Figure 5-4(a) gives the segmental analysis for each building unit. The first one is dodecyltrimethylammonium bromide. It has only two fundamental segments. The long hydrocarbon chain is an attractive segment while the trimethylammonium part becomes a repulsive segment. The former induces an attractive hydrophobic force while the latter induces a repulsive electrostatic force. The second building unit has almost the same molecular structure as the first one. It has the same dodecyl hydrocarbon chain that should become its attractive segment. The difference is on its head group. It still has the trimethylammonium part, but one of the methyl groups is replaced with 2-hydroxyethyl moiety. The hydroxyl group generates a directional force due to its strong capability of hydrogen bonding. This causes this hydroxyl group to be assigned as a directional segment. The trimethylammonium part, however, still has the capability to induce a repulsive force. Hence, it becomes the repulsive segment.

The third building unit, 1,2-dipalmitoyl-*L*-α-phosphatidylcholine, is one of the typical lipid molecules. Like many other lipids and biologically derived molecules, this building unit has a chiral carbon. A chiral carbon is one of the most abundant and prominent parts that can induce asymmetric packing. Thus, this chiral carbon is the asymmetric packing segment of this building unit. This building unit also has two long hydrocarbon chains. Like the first two building units, these hydrocarbon chain parts are the source of the attractive force through their capability of hydrophobic interaction, and thus should become an attractive segment. The phosphatidylcholine part has two charged atoms that are opposite, which makes it zwitterionic. The argument that there might be a possibility that the opposite charges from two approaching molecules can actually generate electrostatic attraction between them is worth some attention. However, when they assemble, it is the attractive hydrophobic force (for this building unit, much stronger than the previous two because of the two long hydrocarbon chains instead of just one) that brings them together. This hydrophobic attractive force is strong enough to align them in a side-by-side mode, in other words, for them not to be significantly out-of-alignment. This will prevent them from being aligned in a way such that they can induce a significant degree of the electrostatic attraction. Therefore, it will be safe to say that the two different charges are at the geometrical positions where they cannot fully attract each other but mostly repel each other. This provides enough incentive to assign the whole phosphatidylcholine group as a repulsive segment. The last building unit is another biologically derived molecule. The dodecyl hydrocarbon chain

(a) Molecular structure of **SA-BU**s



(b) Prediction

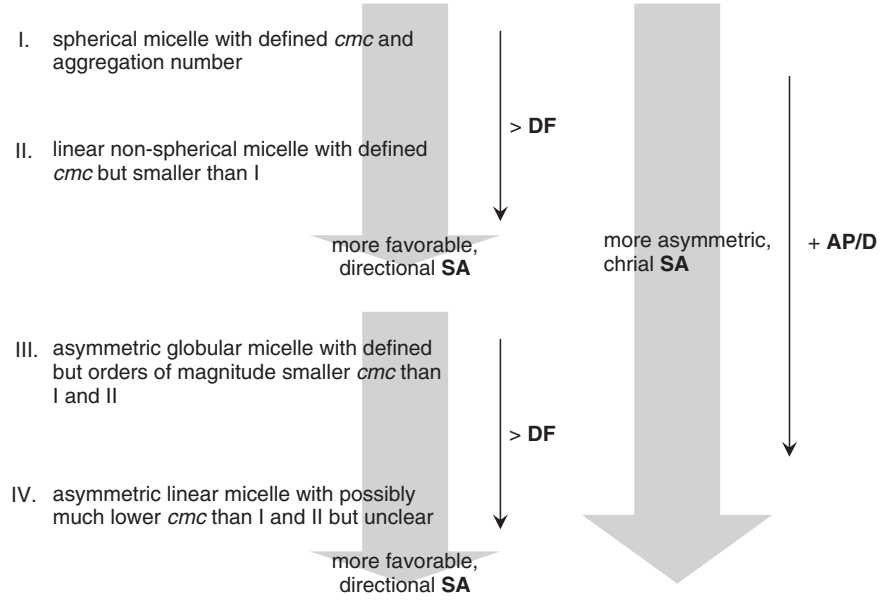

I. spherical micelle with defined *cmc* and aggregation number
II. linear non-spherical micelle with defined *cmc* but smaller than I
> DF
more favorable, directional **SA**
more asymmetric, chrial **SA**
+ **AP/D**
III. asymmetric globular micelle with defined but orders of magnitude smaller *cmc* than I and II
> DF
IV. asymmetric linear micelle with possibly much lower *cmc* than I and II but unclear
more favorable, directional **SA**

Figure 5-4. Prediction of the structure of the primary self-assembled aggregates of different molecular and bio-mimetic self-assembly building units (**SA-BU**) based on segmental analysis: in water at room temperature. **A, R, D**, and **AP** refer to attractive, repulsive, directional, and asymmetric packing segments, respectively. **SA** is short for self-assembly. **DF** refers to directional force. *cmc* is critical micellar concentration.

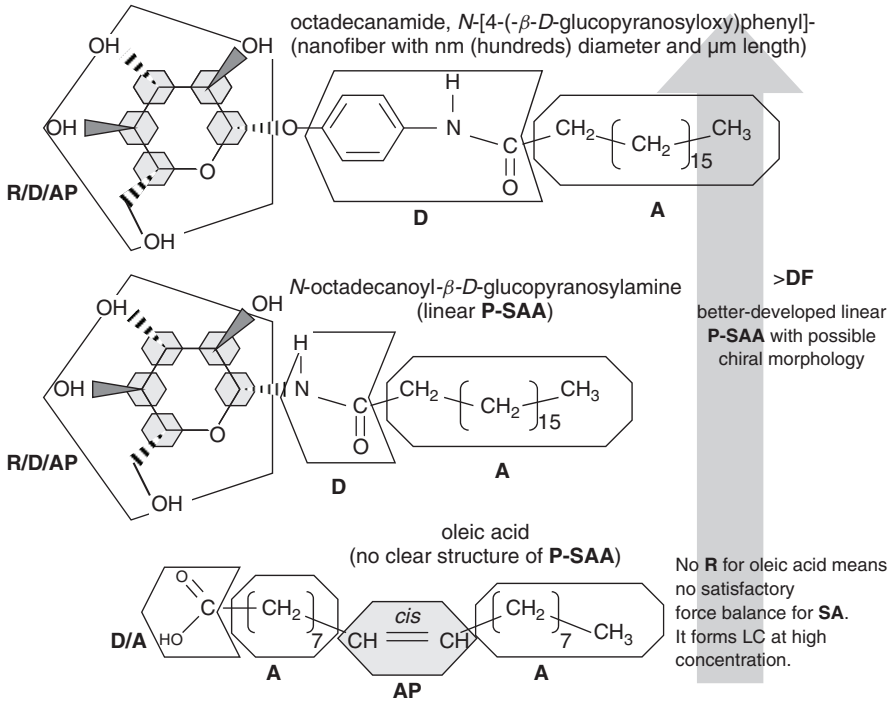


Figure 5-5. Structure of the primary self-assembled aggregate (**P-SAA**) of the self-assembly building units having the same C_{18}-chain but with different segment combination. **A, R, D**, and **AP** refer to attractive, repulsive, directional, and asymmetric packing segments, respectively. **SA** is short for self-assembly. **DF** refers to directional force. LC is liquid crystal.

is its attractive segment. It also has an amide group that is another typical hydrogen bonding group, which makes it a directional segment. The same segmental analysis from Figure 3-8 can be applied here. Now let us take a look at the head group. This is one of the sugar groups (gluconate based). It has four chiral carbons, and all of them should be assigned as an asymmetric packing segment for the same reason as was true for the one in the third building unit. It also has five hydroxyl groups, and all of them are a directional segment because of the hydrogen bonding capability. Lastly, this sugar group is bulky compared with the other head groups from the other three building units. This will be enough to generate some degree of steric repulsion. Thus, this sugar group as a whole is assigned as a repulsive segment.

Figure 5-4(b) shows the prediction of the structures of the primary self-assembled aggregates. It was already confirmed (in the previous two chapters) that the first building unit self-assembles in water at room temperature. This building unit has a classical segmental structure for the symmetric force balance between one attractive segment and one repulsive segment. Therefore, it will be almost inevitable that its primary aggregate will have a spherical morphology. Once the structure of the primary aggregate is predicted to become a well-defined

one, it will be also reasonable to predict that the aggregation number of this primary aggregate will be well-defined. This is exactly the case when this building unit self-assembles in water at room temperature. Numerous literature reports confirm that it forms a spherically shaped micelle with a clearly defined *cmc* (critical micellar concentration) and its aggregation number is well-defined with a relatively narrow polydispersity. The second building unit has a segmental structure identical to the first one except for the one directional segment at the end of it. The force balance between the attractive and repulsive segments should occur as for the first building unit. Without the directional segment, this should induce the same primary aggregate as for the first building unit. When the directional segment comes into play, it will generate hydrogen bonding between the building units, which will induce the directional packing between them. This will promote the primary aggregate to have a strong tendency of directional growth along the direction of hydrogen bonding. At the same time, this directional hydrogen bonding will reinforce the strength of the attractive segment. Comparing it with the first building unit, this segmental structure that has a more attractive segment with a directional segment suggests that the primary aggregate of this second building unit will have a linear type of nonspherical morphology. The *cmc* should be well-defined, but its value should be much lower than the one for the first building unit. The aggregation number should be well-defined as well, and its polydispersity should be narrower than the one for the first building unit. As the directional segment is incorporated into the first building unit, the self-assembly occurs in a more favorable way and at the same time directionally.

For the third building unit, the main focus should be on the asymmetric packing segment. It is clear that its attractive and repulsive segments will be well balanced during self-assembly. The attractive force is much stronger than the previous two building units since it is from the two hydrocarbon chains, but it is well counterbalanced by the double action–like (between the negatively charged atoms and between the positively charged atoms) electrostatic repulsive forces from the repulsive segment. This is at first glance enough to assume that the primary aggregate will have more likely a nonlinear or somewhat globular type of morphology. When considering the role of the asymmetric packing segment, its tendency to arrange the building units in an asymmetric manner might be enough to make the morphology an asymmetric one. However, since this segment does not have a strong directional force, it will not be enough to direct the whole self-assembly process like a directional segment does. Therefore, this segmental structure suggests that the structure of the primary aggregate of this lipid molecule will be a globular one with asymmetric characteristics. Again, the attractive force for this building unit is so strong, which implies that it should show a well-defined *cmc* with the value much smaller, possibly orders of magnitude smaller, than those for the previous two building units. The last building unit has both the directional and asymmetric packing segments in addition to the attractive and repulsive segments. The attractive and repulsive segments will be balanced during self-assembly.

One difference from the previous three building units is that this is not through an electrostatic repulsion but through a nonionic steric force. This gives us an initial

hint that the self-assembly will be more favorable than the previous three building units. In addition, more than one directional segment will reinforce the attractive segment and at the same time direct the whole self-assembly to be a directional one with its tendency much stronger than the second building unit. The same analysis can hold for the role of the asymmetric packing segments. This building unit has four asymmetric packing segments. They first promote the asymmetric packing during self-assembly, which means that the primary aggregates will have a higher chance of being asymmetric and linear. Depending on the delicate changes in overall and local situations, such as a local fluctuation, the four asymmetric packing segments might work in many different combinations. Some of them or even all of them might work cooperatively, or they might work in a counter-cooperative way. If the former is favored under a given condition, it will induce more asymmetric packing, while the latter will do less. Whatever the actual situation might be, the primary aggregate should be reasonably defined with its *cmc* lower than the previous building units. There is a reasonable chance that the *cmc* might be unclear because of the possibility of being highly linear so that the dimensional definition along the direction of its longer axis becomes unclear. When comparing the last two building units, the last one should have more favorable and directional self-assembly since it has a clear directional segment that provides an additional attractive force.

Overall, from the top to the bottom building unit, the general tendency of self-assembly should be more directional and asymmetric. It also will have a high possibility of chiral self-assembly because of the asymmetric packing segments. This issue will be addressed in the next chapter with more details. Shown in Figure 5-4 are representative examples of the structure determination of the primary aggregates. There are numerous different molecular building units in reality. They may have structural characteristics similar to one of the four shown here. They may appear different from any of these four. However, as long as their segmental structures belong to one of the representative types shown here, this general trend of self-assembly can be effective for them as well. The proper choice of a well-documented reference self-assembly system whose primary aggregate is well studied will increase the possibility of more realistic prediction.

5.3.1.2. Molecular Systems II. Now let us take a look at somewhat different examples. Figure 5-5 shows three biologically derived self-assembly building units. At first glance, their structures look quite different, but they are all based on the same length of 18-carbon chains. This subsection attempts to reinforce the argument that was made in the previous subsection by using these more complicated self-assembly systems. The first two building units are from Figure 3-8. As stated in the discussion for that figure, the role of some of their additional segments has been ignored, which was to make some specific issue clearer. This will be thoroughly described in this subsection.

The first building unit is *N*-[4-(-β-*D*-glucopyranosyloxy)phenyl]-octadecanamide. Some segmental analysis was already done for this building unit in Figure 3-8. This is an 18–carbon chain–based building unit. However, the

heptadecyl chain at the far right-hand side of the molecule was identified as an attractive segment. The amide group with a benzene ring was assigned as a directional segment. And the bulky sugar-ring group was a repulsive segment. It is on this repulsive segment that more detailed analysis will be made here. The repulsive segment was based on the bulkiness of this group, which will generate a significant degree of repulsive steric interaction. This sugar-ring group has five chiral carbons, and all of them should be active as an asymmetric packing segment. Compared with the similar multi–chiral carbon head group from Figure 5-4 (example IV), the chiral carbons here are a part of the closed-ring while the one from Figure 5-4 has (linearly) aligned chiral carbons. This structural characteristic might affect the overall packing of the building units somewhat differently from the one in Figure 5-4 since its less flexible nature can limit the degree of potential synergistic or antagonistic interaction between the asymmetric packing segments. However, whatever the final degree of the asymmetric packing might be, it will be strong enough to assemble the building units in an asymmetric manner. The sugar-ring group also has four hydroxyl groups. As clarified in the previous subsection, the hydroxyl group is a typical directional segment because of its hydrogen-bonding capability. Unless the condition for self-assembly directs (or inhibits) their hydrogen-bonding capability otherwise, all four hydroxyl groups should be identified as a directional segment. Therefore, this sugar-ring-based head group should be assigned with three different segments: repulsive, directional, and asymmetric packing segments.

The second building unit is *N*-octadecanoyl-β-*D*-glucopyranosylamine. For the head group of this building unit, exactly the same analysis as for the previous one should be applied. Its direct attachment to the amide group rather than to the benzene group through an oxygen atom should not affect the segmental structure of this sugar-ring group. Just like the previous one, it has three different segments: repulsive, directional, and asymmetric packing segments. As analyzed in Figure 3-8, the heptadecyl chain is the attractive segment of this building unit. And the amide group is another directional segment. Furthermore, as described in the same figure, the degree of the directional force of this amide group will be less than the previous one, which has an additional prominent directional segment (benzene ring).

The third building unit is oleic acid (9-octadecenoic acid, *cis*). Oleic acid is a lipid molecule with a single hydrocarbon chain. Its characteristic structure differs from the previous two building units by the existence of the double bond in the middle of the hydrocarbon chain. Both configurations of *cis*- and *trans*- (commonly known as elaidic acid) are well known. The double bond is located between nineth and tenth carbons. And the molecular geometry of the left-hand side of the double bond is not the same as that of the right-hand side of the double bond. The bulkiness is different and the segmental structure is different as well. This brings us to the only possible conclusion that, whatever the actual configuration might be during self-assembly, the packing between the building units will be always asymmetric. This is why this double-bond group is assigned as an asymmetric packing segment of this building unit. The octyl chain at the end of the building unit is its attractive segment because of its capability to generate an attractive hydrophobic force. And

the heptyl chain in between the double bond and the carboxylic acid group is also long enough to induce an attractive hydrophobic force, and thus is assigned as another attractive segment.

The only part left now is the carboxylic acid group. The carboxylic acid groups for this particular building unit can meet with each other in either a side-by-side or end-to-end mode when they self-assemble in solution. When the attractive segments bring them close enough to be aligned along the direction of the long molecular axis, the carboxylic acid groups will have a greater chance to be aligned in a side-by-side mode. Carboxylic acid groups will then generate the hydrogen bonding through the two different sites of OH— and O—, which will result in the double hydrogen bonding. It will thus strongly drive the direction of the self-assembly, and at the same time strongly attract the building units together. The same scenario should be applied when the carboxylic acid groups are aligned in an end-to-end mode, which can happen when their stronger interaction over the hydrophobic force enforces the interaction between the carboxylic acid groups prior to the hydrophobic interaction. Again, this is the central logic behind the concept of segmental analysis. The two modes might occur together without a significant discrepancy. They might coexist. Separation of the two modes is not what can actually happen in a real system. However, this conceptual approach as if each distinctive segment were interacting separately provides us effective means to understand the self-assembly process and its outcome. The carboxylic acid group now has enough credit to be assigned as both directional and attractive segments of this building unit.

The next step is to estimate the outcome of the self-assembly, that is, the structures of the primary aggregates. Oleic acid does not have a repulsive segment. On the other hand, it has attractive segments that are quite strong, considering the length of the hydrocarbon chain and the strength of hydrogen bond. A segmental structure having strong attractive segments with no repulsive segment simply means that the building units can attract them close to each other but they cannot properly counterbalance the attractive process. An asymmetric packing segment usually does not have significant impact on the balance between the attractive and repulsive segments. It just directs them to be packed asymmetrically. Thus, it can be stated that oleic acid does not have the capability to self-assemble in a given condition. It has a greater chance to keep aggregating until its source runs out. Simply, the concept of force balance cannot be satisfied in this segmental condition. This analysis is well supported in the literature. Reports show that no significant *cmc* can be recorded for oleic acid. Oleic acid forms liquid crystals at high concentration. It would be a reasonable assumption that the overall structure of the liquid crystal is directed by the action of the directional segment.

Case Study 5.1

A study that shows the blood pressure–lowering activity of oleic acid from olive oil (Terés et al., 2008) may reinforce the validity of this approach for the molecular packing based on the segmental analysis. It suggests that oleic acid incorporates into the cell membrane of blood vessels in a way that loosens the molecular packing at the membrane surface, which in turn makes it more

receptive to signals that reduce blood pressure. There is no strong bond (such as a covalent bond) involved during this process. Thus, it can be viewed as a self-assembly process, *with one side of the definition of self-assembly* (for details, refer to Section 1.1), which occurs through the intermolecular interactions between oleic acid and the components within the membrane. The *trans* isomer, elaidic acid, does not show blood pressure–lowering activity. The double bond within elaidic acid should also be assigned as an asymmetric packing segment. However, by taking account of the simple difference in the overall molecular geometry between oleic acid and elaidic acid, it will be reasonable to assume that the asymmetric packing segment from oleic acid will be more strongly expressed than the one from elaidic acid not only when they self-assemble, *also with one side of the definition of self-assembly*, but when they interact with other molecules such as those within the cell membrane of blood vessels as well. Oleic acid is not a major component of the cell membrane. It makes up a very small percentage of it. This seems not enough to induce any significant degree of asymmetric packing on the membrane surface. But it is enough to induce decreased packing of phospholipid head groups locally, which makes the surface loosely packed.

The building unit in the middle has clearly defined attractive and repulsive segments. There is no reason that these two segments cannot be properly balanced. The bulky repulsive segment of this building unit is strong enough to counterbalance the hydrophobic force from the attractive segment. This can also be confirmed by using a reference self-assembly system in which the building unit has a similar yet simpler segmental structure. Some additional attractive features on the repulsive segment should help the self-assembly become more favorable, and the directional segment should make the primary aggregates more likely a linear or circular morphology. Finally, the asymmetric packing segments promote the final morphology to become chiral and/or hierarchical. Notice that this is a typical case for example IV in Figures 5-1 and 5-3. The self-assembly of this building unit should be much more favorable compared with oleic acid and other typical surfactant molecules. And the size and length of the primary aggregates are likely larger and longer than those of nonlinear aggregates.

The building unit on top also belongs to example IV in Figures 5-1 and 5-3. As for the middle one, the attractive segment, which is the hydrocarbon chain, should have no trouble being balanced with the bulky repulsive segment. The additional attractive force from the hydroxyl groups should make this force balance more favorable. The asymmetric packing segments can be assumed to have the same effect on the packing configuration of the building units as for the previous building unit. The directional segment, however, has an additional strong contribution from the benzene ring. This occurs through $\pi-\pi$ interaction between them, which generates a strong tendency of aligning them in a side-by-side mode. Even though the amide group would be out-of-plane at some degree from this benzene ring, the hydrogen bonding from it would not be so antagonistic against the $\pi-\pi$ interaction. Therefore, this segmental structure should result in even more directionally

favorable self-assembly compared with the previous two building units. The primary aggregates should have a better-developed linear morphology than the previous building unit, and its length along the long axis should be longer.

Case Study 5.2

Studies by Jung et al. (2002) and Shimizu et al. (2005) prove that this would be indeed the case for this building unit. They showed that the building unit whose structure is the same as the one shown here but with one more carbon in the hydrocarbon chain self-assembled into a nanofiber with 100–350 nm diameter and micrometer length. One additional methylene group should not cause much difference in the overall force balance during self-assembly. Thus, it would be reasonable to suggest that the building unit shown here also self-assembles into a nanofiber with a similar diameter and length. The length of the nanofiber can be evidence for more prominent directional self-assembly. Also, its diameter is more evidence for more favorable directional self-assembly. They further studied the self-assemblies of a number of different homologue building units whose differences are in the numbers and positions of the *cis* double bonds within the hydrocarbon chains. Based on the segmental analysis made for oleic acid, these *cis* double bonds are the asymmetric packing segments of the homologue series. It is very helpful to see the effects of these additional asymmetric packing segments on their chiral self-assemblies and the asymmetric morphologies of the nanofibers, by following the discussion made in this subsection. Generally speaking, as the more directional segments are involved, the better-developed aggregates with a linear type of morphology are formed. A high ratio of the long axis to the short axis of these nanofibers reflects the fact that its linear morphology originates with the directional segment, and the empty inner space is very likely the result of the chiral asymmetric packing.

Along with the general trend from Figure 5-4, this set of self-assembly systems also proves the validity of the concept of force balance based on the segmental analysis to estimate the morphology of the primary aggregates and to determine the general tendency of their variation as the structures of building units are changed. For the simulation studies of molecular self-assembly that adopted a similar force balance idea, please see McCullagh et al. (2008). It is very intuitive, while reading this article, to track the fundamental balance for the self-assembly, which is the balance between the attractive and repulsive segments. The role of hydrogen bonding in determining the morphologies of the aggregates formed from their biological building units can be understood as a directional segment.

5.3.1.3. Colloidal Systems. Figure 5-6 shows the structure determination of the primary self-assembled aggregates of different colloidal gold particles. Unlike the previous subsection for molecular building units, the structures of the gold colloidal particles (or nanoparticles) are somewhat conceptual. The exact structures of different gold colloidal particles can be varied depending on the individual

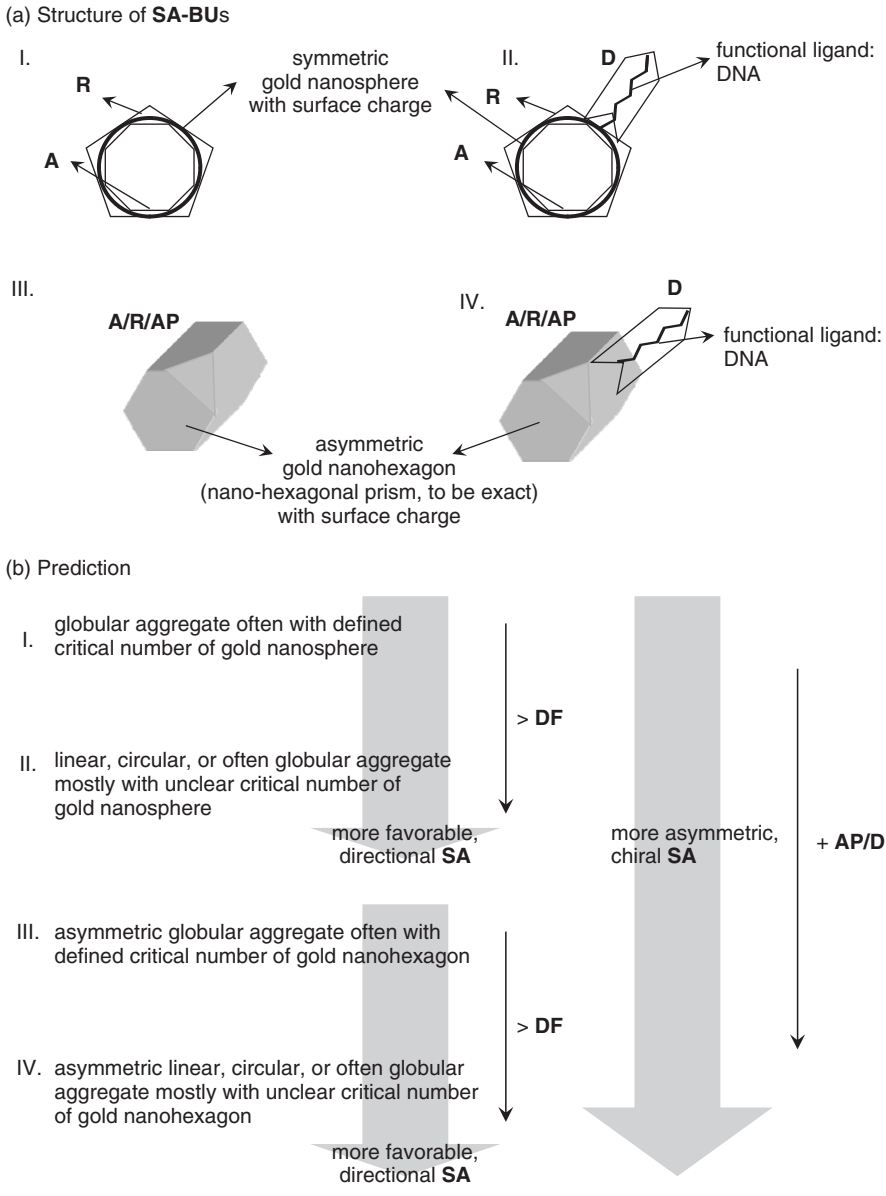


Figure 5-6. Prediction of the structure of the primary self-assembled aggregates of different colloidal gold self-assembly building units (**SA-BU**) based on segmental analysis. **A, R, D**, and **AP** refer to attractive, repulsive, directional, and asymmetric packing segments, respectively. **SA** is short for self-assembly. **DF** refers to directional force.

system. However, as will be seen later, this conceptual approach is effective for understanding the detailed role of each segment and drawing the general trend from it. The numbering with capital letters parallels that in Figure 5-1.

Figure 5-6(a) gives the structures of the gold particles for each example. The first one is a spherical gold colloidal building unit. It has a surface charge. The term *nanosphere* is just to emphasize the notion that its size is in the nanometer range. This simple case of a colloidal particle was already analyzed in Chapter 3. The van der Waals force of the particle is the attractive segment of this building unit. The surface charge, on the other hand, will induce the repulsive force between them through the electrostatic repulsion. Therefore, this is a repulsive segment of this particle. The second building unit is the same gold particle. A difference is that its surface is now modified with a functional ligand. DNA is used in this particular case. DNA is another typical group that can generate directional interaction. Its highly selective attraction between its components is responsible for this. Hence, for this second building unit, the DNA part becomes its directional segment. The attractive and repulsive segments are the same as for the first building unit.

The third building unit is assumed to have a peculiar morphology. This is to express an asymmetric packing segment. Let us assume that there is a hexagonal prism with a short length and it has the capability of self-assembly under a given condition. Its symmetry simply suggests that it will self-assemble through symmetric packing unless the conditional factors strongly oppose it. Now let us assume that one corner of this hexagonal prism is carved out asymmetrically as shown in the figure. The hexagonal prism loses its symmetry completely, which in turn means that, when it self-assembles, it will have a strong chance of being packed asymmetrically. Thus, this becomes the asymmetric packing segment of this building unit. Even though the overall morphology is a hexagonal prism, not a sphere, the attractive segment still should be the van der Waals force and the repulsive segment is the surface charge that induces an electrostatic repulsion. The term *nanohexagon* in the figure is just to point out the fact that its size is in the nanometer range. (It is a hexagonal prism whose size is in the nanometer range to be exact, but, just for the sake of simplicity, hereafter it will be referred to as a *nanohexagon*.) The last building unit is this nanohexagon, which is modified with the same DNA functional group as from the second building unit. It thus has the directional segment in addition to the attractive, repulsive, and asymmetric packing segments.

With these segmental analyses, let us now attempt to make the general prediction concerning the morphology of the primary aggregates that are formed from each of the building units. Figure 5-6(b) presents this. It also shows that the morphology changes in the primary aggregates can be tracked by following the segments of each building unit. The numbering with capital letters parallels that in Figure 5-6(a). It also parallels the numbering in Figures 5-1 and 5-3. It is assumed that the condition is in water at room temperature.

The first gold building unit was a nanosphere with a surface charge. As discussed in Figures 3-5 and 3-6, as long as the experimental condition is not against

it, this colloidal building unit should self-assemble into a well-developed self-assembled aggregate. It does not have an asymmetric packing segment; thus the force balance between the attractive and repulsive segments will be symmetric. This yields an aggregate with a globular type of morphology. The average number of gold nanospheres within each aggregate (aggregation number) and the *can* (critical aggregation number), which is the number concentration of gold nanospheres at the point where the self-assembly occurs, should be clearly defined. And it is, in most cases, proven in the literature. The second building unit was the same gold nanosphere but with DNA ligand. This directional segment does not disrupt the symmetric force balance between the attractive and repulsive segments. But it directs the whole force balance toward the direction that is favored by the interaction between the ligands. It will also provide some additional attractive force, which is actually the main driving force for this directionality.

The schematic description in Figure 5-3 shows that this segmental structure should be favorable for the formation of a linear or circular type of primary aggregate. For this particular case, however, it can be changed. Depending on the actual number of the directional segment and its position on the surface of the gold nanosphere, it can form other types of morphologies, too. If a large number of the DNA directional segments are evenly distributed on the surface of the gold nanosphere, the morphology of the aggregate can be close to globular, which is usually formed from the colloidal building units without a strong directional segment. If, however, a relatively small number of the DNA directional segments happen to be positioned on the two opposite sides of the gold nanosphere, a linear network might be a more likely morphology for the aggregate. In most cases, the aggregation number is not well-defined. If the DNA directional segment happens to have the right condition so that it is well balanced with the attractive and repulsive segments during the self-assembly, this system is likely to have a well-developed *can* as for the first building unit. And its aggregation number should be bigger than that of the first building unit. Its *can* should be lower. Otherwise, it is highly likely that the self-assembly will continue until all of the DNA groups are consumed. When comparing the first and second building units, as the directional force is incorporated, the colloidal self-assembly becomes more favorable and directional, just do for molecular self-assembly. The changes in the morphologies of the primary aggregates are tracked according to the same concept, too.

The third building unit was an asymmetrically shaped gold nanohexagon with a surface charge. Again, the schematic description in Figure 5-3 shows that this segmental structure should favor an asymmetric globular type of primary aggregate. When the condition is right, the *can* should be well-defined. But it can also be suggested that the existence of the capillary force (which is a colloidal force and comparable with the other intermolecular forces) more likely takes over the force balance during self-assembly. This will be especially the case when the long axis of the nanohexagon is longer. When this becomes the situation, the self-assembly will be continued until all of the nanohexagons are consumed. Whatever the actual condition of the gold nanohexagon might be, the chirality of the primary aggregate should be expressed as a whole or at least locally within the aggregate.

The last building unit was asymmetric gold nanohexagon with the DNA directional segment. The same logic should be applied for the primary aggregate. Its segmental structure should yield a linear or circular type of morphology with a well-defined asymmetric character. However, depending on the DNA condition, it could also yield a globular or networked type of morphology. As in the second example, the *can* is not clearly defined. If the condition, mainly the DNA condition, happens to be the right one, there will be a *can* with an aggregation number bigger than that of the third building unit. And its *can* should be lower than that of the third building unit. When comparing the third and the last building units, as for the first two, as the directional segment is increased, the self-assembly of the gold nanohexagon becomes more favorable and directional, again just as in molecular self-assembly.

Overall, when the asymmetric packing and directional segments are incorporated within colloidal building units, the self-assembly occurs in a more asymmetric manner and, in many cases, has a higher possibility of chiral self-assembly. What it takes is a proper segmental analysis of these somewhat complicated building units.

Case Study 5.3

Nelson and Braun (2007) review the directional self-assemblies of the colloidal particles whose directional interactions are acquired by the preferential modification of their surfaces, including DNA. DNA ligands also provide the attractive force for these self-assemblies. They further explain the critical impact of the ligand positions on the colloid surfaces on the morphologies of their aggregates. Implications of these directional colloidal self-assemblies for future applications and the challenges are well described. Goyal et al. (2008) report a theoretical study of the self-assembly of the dipolar colloidal particles (colloidal particles with permanent dipole moments on the two opposite sides) in a high-dielectric solvent. The self-assemblies are directional and the directional forces are induced by the dipole–dipole interactions. They observed the critical behaviors during these colloidal directional self-assemblies and the aggregation numbers. The formation of the higher-order aggregates and their morphologies are clearly explained as well.

Case Study 5.4

Another fascinating result (Zerrouki et al., 2008) that reports the formation of chiral chains through self-assembly of colloidal dumbbells provides a very realistic example of the argument that was made in this subsection. When the symmetric dumbbells (two silica nanoparticles of similar size joined by iron oxide) self-assemble under an external magnetic field, they form a chain that shows a symmetric overall morphology. When the asymmetric dumbbells (two silica nanoparticles of different sizes joined by iron oxide) self-assemble also under an external magnetic field, they form a chain that shows a helical structure.

For both colloidal self-assembly building units, the induced dipole–dipole interaction is their attractive segment and the steric repulsion is their repulsive segment. The balance between these two forces is the driving force for their self-assembly. The iron oxide part in both building units is their external force–specific functional segment (see Subsection 1.2.2.2 for details about this segment) since it is the part that is interacting with the external magnetic field directly. The external magnetic field also offers an additional attractive segment to the dumbbells through the magnetization of the iron oxide part. For the asymmetric dumbbell building unit, it is its structure that becomes the asymmetric packing segment, which induces the asymmetric packing during the self-assembly (asymmetric self-assembly) that eventually gives the asymmetric morphology to the aggregate (chiral chain). The symmetric dumbbell does not have any asymmetric packing segments, which can be explained by the main logic that its aggregate is a symmetric chain that is formed through a symmetric self-assembly.

A follow-up simulation study (Keaveny and Shelley, 2009) reveals a more quantitative relation of the handedness of the chiral aggregates with the structural parameters, which include the size ratio of the two dumbbells (which can be viewed as the degree of asymmetric packing capability), the aggregation number of the aggregates, and the strength of the external magnetic field.

Case Study 5.5

A simulation study by Nguyen et al. (2008) that shows the effect of the structures of tethered nanoparticles (aspect ratio and asymmetry) on the local packing during their self-assembly is another good example that supports the argument made here. They further show that the chiral self-assembly of the nanoparticles is induced by the symmetry breaking, which eventually generates the morphological chirality of the self-assembled aggregates. The assembly patterns vary in a systematic way by responding to the changes in the attractive and repulsive forces between the nanoparticles. They also show that the primary aggregates self-assemble into the higher-order aggregates as the concentration of the nanoparticles is increased. The effect of the changes in the attractive and repulsive forces between the primary aggregates on this secondary self-assembly is very intuitive to read, regarding the discussion that will be made in the next subsection.

5.3.2. Higher-Order Self-Assembled Aggregates

Figure 5-7 shows the schematic explanation for the morphological changes in higher-order self-assembled aggregates for each example in Figure 5-2. The solid-line arrow on the far left-hand side for all four examples indicates the self-assembly prior to the current one. For all examples, it is assumed that the current self-assembled aggregates are the secondary aggregates. The bold dotted-line arrow on the far right-hand side is for the possible tertiary aggregates. To make the explanation clearer, the building units for all examples come from Figure 5-3.

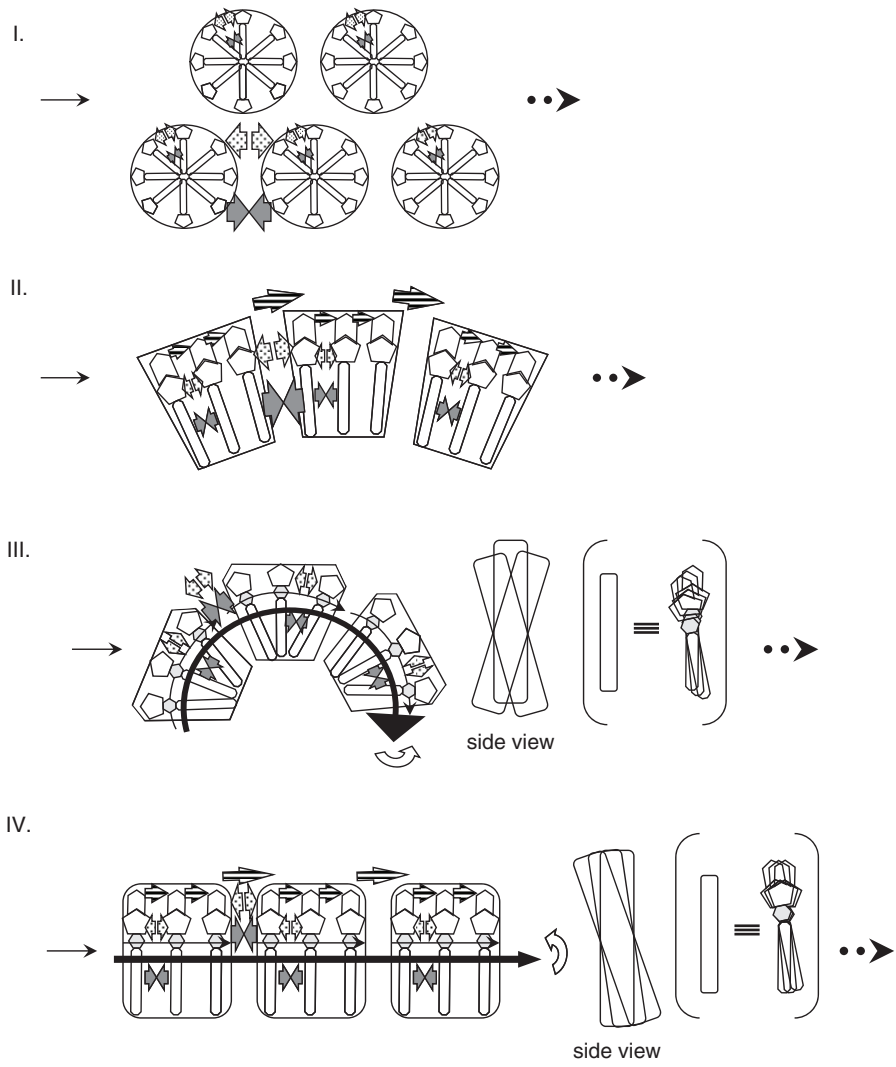


Figure 5-7. Schematic explanation of the structure identification of the higher-order self-assembled aggregate of a given self-assembly building unit.

For the first example, it may be the simplest description to say that the spherically shaped primary aggregates continue into the secondary self-assembly through the force balance between the attractive and repulsive segments of the primary aggregates. It is assumed here that the attractive segment is generated through the increase of the total concentration of the primary aggregates. However, as discussed in the previous chapter, there are many different ways to achieve this segmental condition. Whatever the way might be, the attractive–repulsive interaction between the primary aggregates can be assumed to be symmetric by ignoring the possible

local fluctuation. This is reasonable because of its (local fluctuation) much faster dynamics compared with those of the primary aggregates. The morphology of the secondary aggregate will have a higher chance of being nonlinear or globular.

The second example is also when the primary aggregates, nonlinear in this case, self-assemble into the secondary aggregates through the interaction between the attractive and repulsive segments of the primary aggregates. One difference is that the directional segment of the primary aggregates is now involved. This directional segment acts between the primary aggregates so that it directs the entire morphology of the secondary aggregates, which will make it most likely a linear or circular one.

The third example has an asymmetric packing segment. This additional segment packs the primary aggregates into an asymmetrical geometry. The side view shows it more clearly. The direction of the asymmetric packing is mainly dependent on the nature of the asymmetric packing segment itself. But it is reasonable to suggest that eventually the secondary aggregates will have a linear or globular type of morphology.

The final example has both the directional and asymmetric packing segments in addition to the attractive and repulsive segments. This directional segment working between the primary aggregates will direct the formation of the secondary aggregates, and at the same time work cooperatively with the asymmetric packing segment. The side view is also shown. This segmental condition is ideal to produce highly diverse asymmetric morphologies such as linear, circular, or helical. The two side views for examples III and IV also show the possible difference that can be caused by the action of the directional segment on asymmetric packing. When the asymmetric packing segment works without the directional segment, it can be a directional packing but it can have some degree of periodic packing as well, such as a zigzag way. On the other hand, when it works in the presence of the directional segment, it is more likely that the packing of the primary aggregates mainly occurs in a directional manner.

5.3.2.1. Molecular Systems. Figure 5-8 shows how to apply the schematic illustration from the previous figure to the actual higher-order self-assembled aggregates. This, in other words, is how to apply the segmental analysis of primary self-assembled aggregates to predict the morphologies of the higher-order aggregates. It is for molecular and biologically derived self-assembly building units, which are exactly the same as in Figure 5-4(a) with parallel numbering with capital letters.

Dodecyltrimethylammonium bromides, the first example, will eventually form liquid crystals as they are imposed under the condition of an additional attractive segment between the primary aggregates (micelles), such as the increasing of their concentration. The symmetric interaction between the attractive and repulsive segments should make the secondary aggregates mainly a globular morphology. The literature, however, shows that there are many more different morphologies that do not merely originate from the plain assembly of the primary aggregates. This can be understood as a result of the *post-force balance* within the secondary

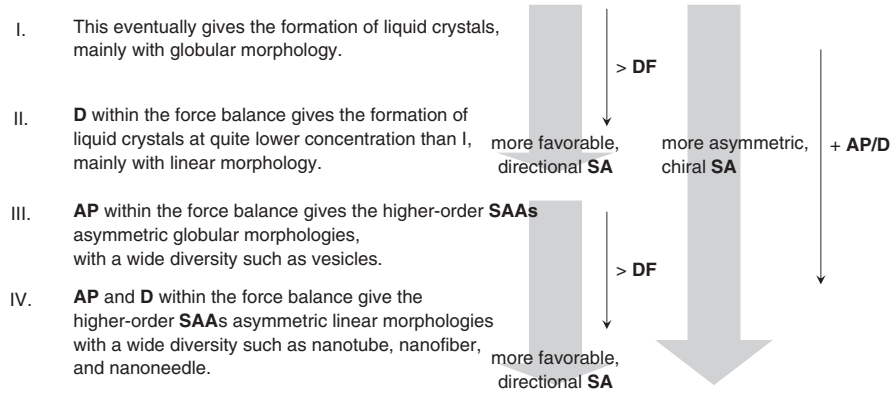

I. This eventually gives the formation of liquid crystals, mainly with globular morphology.
II. D within the force balance gives the formation of liquid crystals at quite lower concentration than I, mainly with linear morphology.
III. AP within the force balance gives the higher-order SAAs asymmetric globular morphologies, with a wide diversity such as vesicles.
IV. AP and D within the force balance give the higher-order SAAs asymmetric linear morphologies with a wide diversity such as nanotube, nanofiber, and nanoneedle.
> DF
more favorable, directional SA
more asymmetric, chiral SA
+ AP/D
> DF
more favorable, directional SA

Figure 5-8. Prediction of the structure of the higher-order self-assembled aggregates of different molecular and bio-mimetic self-assembly building units based on segmental analysis: in water at room temperature. For all four examples, what is shown is the secondary self-assembled aggregates. **D** and **AP** refer to directional and asymmetric packing segments, respectively. **SA** and **SAA** are short for self-assembly and self-assembled aggregate, respectively. **DF** refers to directional force.

aggregates, which often occurs during the assembly of the primary aggregates or immediately after the formation of the secondary aggregates. As the concentration of the building units is further increased, a higher-order self-assembly such as tertiary might be overlapped by the previous self-assembly; that is, the distinction between the different orders of self-assemblies becomes unclear. The most typical structures of these higher-order aggregates, including hexagonal, cubic (with different symmetries), and lamellar morphologies, can be considered as a result of this overlapped self-assembly process. Each structure is the structure that fits best with the force balance condition given by the concentration condition. The directional segment at the head group of the second example in Figure 5-4(a) can also work as a directional segment of the primary aggregates during the secondary self-assembly, as the condition favors it. Since this directional segment works not only to direct the secondary self-assembly but to give an additional attractive segment as well, the overall force balance should be favorable for the formation of liquid crystals but at much lower concentration than the one for example I. The morphology of the secondary aggregates should be much more linear with a wide range of diversities.

The third example, lipid molecule, has an asymmetric packing segment. This asymmetric packing segment can work on the primary aggregates when they self-assemble. The primary aggregate is a result of the primary building units (lipid molecules) packed asymmetrically. It thus possesses an asymmetric nature unless there is a condition that works against it. This asymmetric nature of the primary aggregates is its asymmetric packing segment, which should provide the asymmetric characteristics to the morphology of the secondary aggregates formed by the secondary self-assembly. Since there is no directional segment, it is highly likely that it will have a globular type of morphology with a wide range of diversities. The

last example has both the asymmetric packing and directional segments. With the same logics from the previous examples II and III, both of these segments should be present on the primary aggregates when the condition favors the secondary self-assembly. The result should be the secondary aggregates with a linear type of asymmetric morphology. Nanotubes, nanofibers, and nanoneedles are commonly found types as proven in many studies.

The general trend for the formation of the higher-order aggregates now looks the same as the one from Figure 5-4(b). As the directional segment is increased, the higher-order self-assembly becomes more favorable and directional, as is true for the primary self-assembly. As both the asymmetric packing and directional segments are increased, the higher-order self-assembly becomes more asymmetric and chiral, again as is true for the primary self-assembly. The concept of segmental analysis works well for the higher-order self-assemblies.

Case Study 5.6

There is a study that reviews the self-assembly and the morphologies of the self-assembled aggregates of the amphiphiles that have embedded biological functionalities (Berti, 2006). It will be very instructive in terms of applying the general trend that was established in this subsection, while reading this article, to capture the central idea of the balance between the hydrophobicity from the hydrocarbon chains and the hydrophilicity from the head groups of the bio-mimetic building units to understand their self-assembly. A role of the directional segment is also implied. And it will be also instructive to identify the asymmetric packing segment of each building unit and its role in determining the morphology of the aggregates. The notion of an external force–specific functional segment is mentioned as well.

Case Study 5.7

Another review article that discusses the self-assembly of oligopyridine molecules is also very instructive in this sense (Ziener, 2008). Their self-assembly occurs, both in bulk solutions and at surfaces, through multi-step processes (in terms of the definition of self-assembly in this book), which generates a variety of hierarchically ordered self-assembled structures. van der Waals and hydrophobic interactions are the attractive segments for their self-assembly. And the parts within the oligopyridine molecules that have the capability of hydrogen bonding and of coordination bonding with additional metal ions are their directional segments that are responsible for their directional self-assembly.

5.3.2.2. Colloidal Systems. Figure 5-9 discusses the same logic as Figure 5-8 but with colloidal building units. Each building unit is exactly the same as the one in Figure 5-6 with parallel numbering with capital letters. For all four it will be assumed that the increased concentration of gold colloidal particles, that is,

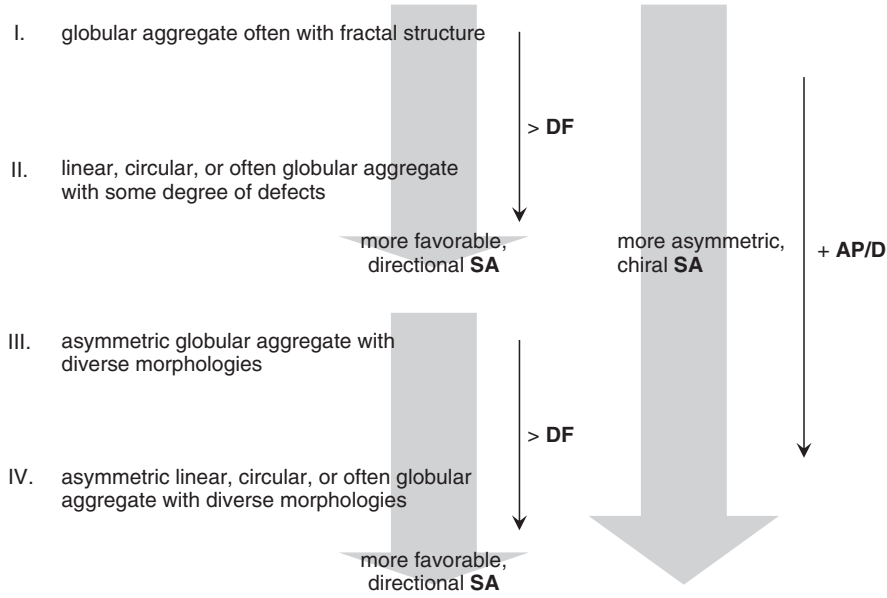

I. globular aggregate often with fractal structure
> DF
II. linear, circular, or often globular aggregate with some degree of defects
more favorable, directional SA
more asymmetric, chiral SA
+ AP/D
III. asymmetric globular aggregate with diverse morphologies
> DF
IV. asymmetric linear, circular, or often globular aggregate with diverse morphologies
more favorable, directional SA

Figure 5-9. Prediction of the structure of the higher-order self-assembled aggregates of different colloidal gold self-assembly building units based on segmental analysis. **D** and **AP** refer to directional and asymmetric packing segments, respectively. **SA** is short for self-assembly. **DF** refers to directional force.

the primary building units, induces the additional attractive segment between the primary aggregates.

For example I, since there are no other segments but the attractive and repulsive segments within the primary aggregates of the spherical gold particles, there is no reason that they cannot self-assemble through the symmetric interaction between their attractive and repulsive segments. And this should promote the secondary aggregates to have a globular type of morphology. Because the primary colloidal aggregates are dynamic objects (as for the molecular aggregates) and because they are less dense than the molecular aggregates due to the geometrical constraint of colloidal particles, the degree of rearrangement of individual particles is higher than for molecular aggregates even during secondary self-assembly. This could be the reason that the secondary aggregates of this example often show fractal structures. In example II, the segmental structure should not be much different from the one in example I except for the existence of the directional segment. This directional segment will work to make the secondary self-assembly more favorable than in example I, and the morphology of the secondary aggregates will be more directionally grown types such as linear and circular. A globular morphology is often formed, which again could originate from the dynamic nature of the colloidal aggregates. Whatever the final morphology might be, the degree of structural defects is usually less than for the one of example I because of the action of the directional segment.

In the third example, the asymmetric packing segment within the gold nanohexagon generated the asymmetrically packed primary aggregates. Even though this is a less dense colloidal aggregate, the asymmetric nature of the primary aggregates should be preserved at least to some degree when they go into the secondary self-assembly. This is the same logic as for the molecular aggregates in Figure 5-8. However, the possibility that the asymmetric nature of the primary aggregates is relaxed out during and even before the secondary self-assembly would be much higher than the molecular aggregates. Generally, it is safe to say that the secondary aggregates favor having asymmetric globular morphologies, but there is some possibility of their being symmetric globular morphologies. In any case, this possible disappearance of the asymmetric packing segment during the secondary self-assembly will surely increase the morphological diversities. The last example has both the asymmetric packing and directional segments within the primary building unit. With the discussion just made for examples I and II, the directional segment will surely work for the assembly of the primary aggregates, but the role of the asymmetric packing segment could be reduced. Therefore, the morphology of the secondary aggregates would be mainly of an asymmetric linear or circular type. But it could be symmetric globular aggregates as well, if the asymmetric packing nature is lost. For any morphology, its diversity should be rich for the same reason as in example III.

The general tendency is the same as for Figure 5-6(b). The increasing of the directional segment induced more favorable and directional secondary self-assembly. The incorporation of the asymmetric packing segment along with the directional segment made the secondary self-assembly more asymmetric and chiral. Higher-order self-assemblies beyond the secondary self-assembly are rare for colloidal building units. There may be some, but mostly they tend to be easily overlapped with lower-orders of self-assemblies.

5.4. COLLECTION OF THE STRUCTURES OF SELF-ASSEMBLED AGGREGATES

5.4.1. Primary Self-Assembled Aggregates

Table 5-1 lists the collection of various structures that have been experimentally identified for the primary self-assembled aggregates. They are the ones that frequently appear in the literature. Table 3-1 lists the collection of the names and descriptions of various primary aggregates. Whenever one of these structures is referred to self-assembled aggregate, it is very likely that it is a primary aggregate. Then, by cross-checking with Table 3-1, more details of the nature and type of the aggregates can be acquired. Also, this way, the type of self-assembly building unit from which each structure is most likely obtained can be determined. For example, according to Table 3-1, any building units that have the attractive and repulsive segments can self-assemble into micelle, reverse micelle, or microemulsion. Then, Table 5-1 says that, without any additional segments, their structures will be most likely a sphere. Table 5-1 also says that when they acquire a directional

TABLE 5-1. Collection of various structures of the primary self-assembled aggregates that are shown in Table 3-1 and the segment combination of the building units with which each structure is most likely obtained. A, R, R^c, D, and D^c refer to attractive, repulsive, conditional repulsive, directional, and conditional directional segments, respectively. ED is external force–induced directional factor.

Structure	Self-Assembled Aggregate	Segment Combination of Building Unit
sphere	micelle, reverse micelle, microemulsion, macroemulsion, double emulsion,	only **A** and **R**
rod	micelle, reverse micelle, microemulsion, hemimicelle, semimicelle	with **D** or $\mathbf{D}^c$
disk	micelle	with **D** or $\mathbf{D}^c$
ellipsoid	micelle	with **D** or $\mathbf{D}^c$
spheroid (prolate, oblate)	micelle	**R** with relatively strong **A**
hollow sphere	vesicle, liposome, niosome	**R** with strong **A**
microcapsule	vesicle, liposome, niosome	**R** with strong **A**
foam-like	foam	with **A** and **R**
finger-like	Langmuir monolayer	with **A** and **R**
planar sheet	monolayer, film, adlayer	any one on substrate
narrow strip	Langmuir-Blodgett (LB) film	with **ED**
island-type	adlayer, vapor-deposited film	with **A** and $\mathbf{R}^c$
circular	surface micelle, Langmuir monolayer	with **A** and **R**
ring	Langmuir monolayer	with **A** and **R**

or conditional directional segment, it is now most likely that the structures of their primary aggregates become rod, disk, or ellipsoid. For the definition and function of conditional directional segments, see Subsection 1.5.2. Subsection 1.5.1 gives the details for conditional repulsive segments. For the external force–induced directional factor, refer to Subsection 1.2.2.2.

Combined use of Table 5-1 with Table 3-1 can help us understand why a certain type of structure is preferred for a certain type of primary aggregate, which in turn can provide a practical idea of how to control the structures of the primary aggregates. As will be shown in the third part of the book, the ability of controlling the structures of the primary aggregates is directly related to the ability of controlling the nanoscale structures for many nanotechnology systems. For example, it was described in Section 3.4 that, by tuning the sizes and types of micelles, the sizes and properties of spherical nanostructures can be controlled. Now, by controlling the structures of the primary aggregates in addition to these controls, the detailed morphologies of the nanostructures can be tuned as well. The implication of these nanostructural controls for the nanoproperties will be discussed in Chapter 12.

5.4.2. Higher-Order Self-Assembled Aggregates

Table 5-2 lists the collection of various structures that have been experimentally identified for the higher-order self-assembled aggregates. As with the primary aggregates, these are the ones that frequently appear in the literature. The structures of the higher-order aggregates are more diverse and can be trickier to detect

TABLE 5-2. Collection of various structures of the higher-order self-assembled aggregates that are shown in Tables 4-1 and 4-2, and the segment combination of the building units with which each structure is most likely obtained. A, R, D, D^c, and AP refer to attractive, repulsive, directional, conditional directional, and asymmetric packing segments, respectively. ED is external force–induced directional factor.

Structure	Self-Assembled Aggregate	Segment Combination of Building Unit
crystal-like	mesophase, reverse mesophase, colloidal crystal	with **A** and **R**
random chaotic	gels (hydrogel, organogel, xerogel)	with **D** and **AP**
fibrous	fibers	with **D** and **AP**
multiple rings	vesosome, mesosome	with **A** and **R**
twisted rod	J-aggregate, actin, collagen	with **A, R,** and **D**
hollow tube	microtubule	with **A, R, D,** and **AP**
tubular	J-aggregate	with **A, R,** and **D**
columnar	H-aggregate	with **A, R,** and **D**
chain-like	colloidal chain, protein chain, polymer-micelle chain	with **D,** $\mathbf{D^c}$, or **ED**
dendritic	Langmuir monolayer (at high surface pressure)	with **D** or $\mathbf{D^c}$
fractal	some colloidal crystals	with **A** and **R**
helical rod	actin, collagen	with **A, R, D,** and **AP**
α-helix	polypeptide chain, RNA	with **A, R, D,** and **AP**
double helix	DNA	with **A, R, D,** and **AP**
ribbon	some bio-mimetic aggregates, some hetero-agggregates	with **A, R, D,** and **AP**
multiple sheets	Langmuir-Blodgett (LB) film, multilayered films	with **A** and **R**
folded-chain	proteins	with **A, R, D,** and **AP**
branched rod (tree-like)	Liesegang ring	with **A, R, D,** and **AP**
multiple stack (pyramidal-like)	vapor-deposited film	any one with **A**
hetero-strip	multicomponent vapor-deposited film	any one with specific **A**
dimeric	J-aggregate, H-aggregate	with **A, R,** and **D**
trimeric	J-aggregate, H-aggregate	with **A, R,** and **D**
multimeric	J-aggregate, H-aggregate	with **A, R,** and **D**

than those of the primary aggregates. There are a number of structures that are identified from the same higher-order aggregate but referred to by different names in different reports. Those are not included in Table 5-2. This is mainly because the nature of the higher-order self-assemblies is more diverse and flexible than that of primary self-assemblies, and many higher-order aggregates originate from biological systems. This often makes the identification of the higher-order aggregates difficult. But whenever one of the structures listed in Table 5-2 is identified for self-assembled aggregate, it is quite likely that it is a higher-order aggregate.

Table 5-2 also lists the names of aggregates that would most likely reveal each of the higher-order structures. By referring to this information along with that in Tables 4-1 and 4-2, the lower-order aggregates can be identified as well. This can help us grasp a better picture of the whole assembly processes of a given assembly system. Also, by cross-checking against Tables 4-1 and 4-2, more details for the

higher-order aggregate and the type of building unit from which each higher-order structure is most likely obtained can be determined. For example, Table 4-1 says that any building units that have attractive and repulsive segments (under the right condition) can multi-self-assemble into mesophases or reverse mesophases, and their lower-order aggregates are micelles or reverse micelles, respectively. Then, Table 5-2 says that their overall structures are probably crystal-like. This can help us understand the structural and physical properties of the aggregate, and help us choose proper characterization techniques. Table 5-2 also can help us study the likely structural changes when there are changes in the building units. With the same mesophase or reverse mesophase, if the building unit acquires directional and asymmetric packing segments, it is now random chaotic or fibrous structures that would be most likely revealed for the higher-order aggregates.

As for the primary aggregates in the previous subsection, combined use of Table 5-2 with Tables 4-1 and 4-2 can help us understand why a certain type of structure is preferred for a certain type of higher-order aggregate, which in turn can provide a practical idea of how to control the structure of the higher-order aggregates. As will be shown in the third part of the book, the ability for controlling the structures of the higher-order aggregates along with those of the primary aggregates offers the facile ability to control the structural properties of many nanotechnology systems. For example, the previous subsection described how the sizes, properties, and detailed morphologies of nanostructures can be tuned by controlling the structures of the primary aggregates. And Section 4.4 described how the design of the overall arrangement and hierarchy of the nanostructures is directly related to the structures of the higher-order aggregates. Now, by acquiring the ability to control the structures of the higher-order aggregates, the design of diverse multi-order nanostructures (hierarchical nanostructures) can become more systematic. Hierarchical nanostructures have so much importance for the actualization of many promising nanoproperties. Chapter 12 has more details for this. When the nanostructures that are developed by using the self-assembled aggregates are nanopore-based ones, those aggregates are commonly called a *template* (a soft template as opposed to a hard template), *porogen*, or *structure-directing agent*.

5.5. SUMMARY

The main question for this chapter was how the structures of the self-assembled aggregates can be controlled in a practical manner. The chapter showed that:

1. A systematic analysis of the structures of the building units is a key to the control of the self-assembled aggregates regardless of their structural orders.
2. The role of directional and asymmetric packing segments is crucial for the structural diversities of the higher-order aggregates.
3. This approach is effective for different types of building units.

For many biological building units, the orders of their self-assembly can go much higher than those for nonbiological building units. Moreover, they often

take multiple different self-assembly paths during the higher-order self-assemblies, which provides much more diverse morphological natures for their aggregates. This is important for the proper expression of their biological functionalities in a real system. Properly addressing this issue based on the structural analysis of the building units is necessary when we deal with them. This issue will be examined in the next chapter.

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6

Hierarchy and Chirality of Self-Assembled Aggregates

6.1. ASSEMBLY ISSUE

The three previous chapters discussed how the systematic structural analysis of self-assembly building units (*segmental analysis*: see Subsection 1.2.2 for the details) can be applied to a number of different self-assembly issues. It was useful for the determination of the self-assembly capability of a given building unit, for the determination of the multi-step self-assembly capability of the building unit, and for the determination of the overall structures of the self-assembled aggregates with different structural orders. This chapter will follow up on these issues with a question about the two important structural characteristics of the self-assembled aggregates. The main question to ask here is:

Will your self-assembled aggregate have hierarchy, chirality, or both?

There are many other structural characteristics for aggregates. And each structural parameter can be a unique one for each aggregate. However, hierarchy and chirality are the two most important and most often encountered ones in a wide range of self-assembly systems. Also, they are the ones that can provide a large amount of unique physical and chemical properties for aggregates. At the same time, there are many different means and routes that can be used to control them. This makes the hierarchy and chirality of aggregates very useful in a wide range of applications, especially in the areas of nanotechnology and biotechnology.

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This chapter develops a proper segmental analysis of how to determine the hierarchy and chirality of a given aggregate. It shows that the same structural approach from the previous chapters stands valid for it. Issues regarding their applications will be discussed in third part of the book. They include when this specific structural information is needed, why they are so important for a certain nanotechnology system, and how to apply them.

6.2. GENERAL OVERVIEW

Self-assembled aggregates, regardless of their structural orders and formation conditions, are formed as a result of the interactions between weak intermolecular and colloidal forces. In other words, this means that all of the aggregates are a dynamic object. Thus, the hierarchy here implies any order of aggregates whose structures consist of at least two different orders of building units. For example, and in most cases, they consist of the primary and secondary building units. For many biological aggregates, it is not uncommon that the hierarchy appears as a result of multi-orders of assembly. Furthermore, hierarchy is not a permanent structural characteristic for any of the aggregates. There can be hierarchy right after the formation of a certain aggregate, but it could be soon relaxed out to have non-hierarchy. Hence, just because a self-assembly system can go through multi-step assembly processes, it does not necessarily mean that its aggregates have hierarchy. Hierarchy in aggregates should not be confused with that in other systems, such as dendritic polymers that are synthesized via strong bond. The same logic goes for chirality. When a certain primary building unit has a chiral center, it has chirality. Its chirality is permanent throughout the entire orders of self-assembly. Meanwhile, when it forms an aggregate whose morphology shows chirality, this morphological chirality is now not a permanent one. It could also be relaxed out depending on the condition. However, despite all these possible disruptions, in most self-assembly systems, hierarchy and chirality are surprisingly resilient. They are well preserved not only for thermodynamic aggregates but for kinetically stabilized aggregates as well. This is another feature where the power of weak intermolecular and colloidal forces comes into play.

Figure 6-1 shows a general overview of the identification of the hierarchy and chirality of aggregates of a given building unit. The first question to ask is whether the primary building unit has at least one asymmetric packing segment. If the answer is no, the primary aggregates that are formed from it have a very strong possibility of showing no chirality at all. Its overall morphology will be highly symmetric. The question to ask next is whether the building unit has the capability of multi-step self-assembly. If the answer is no, it can form only the primary aggregates with no hierarchy and no chirality. This is *example I*. If the answer is yes, there will be higher-order aggregates that will most likely preserve their hierarchy. But no morphological chirality will be expressed. This is *example II*. If the answer to the question about the asymmetric packing segment of the primary building unit is yes, then the primary aggregates will have a very strong possibility

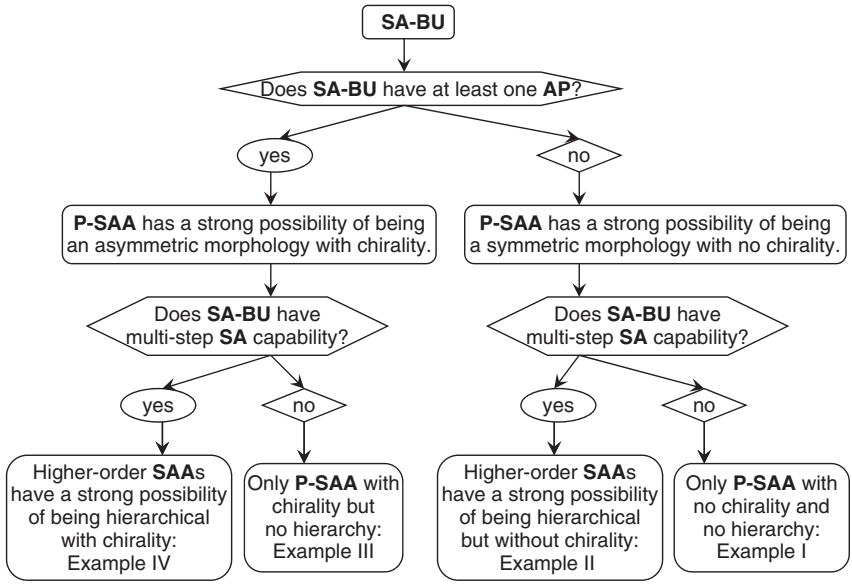

SA-BU
Does SA-BU have at least one AP?
yes
no
P-SAA has a strong possibility of being an asymmetric morphology with chirality.
P-SAA has a strong possibility of being a symmetric morphology with no chirality.
Does SA-BU have multi-step SA capability?
Does SA-BU have multi-step SA capability?
yes
no
yes
no
Higher-order SAAs have a strong possibility of being hierarchical with chirality: Example IV
Only P-SAA with chirality but no hierarchy: Example III
Higher-order SAAs have a strong possibility of being hierarchical but without chirality: Example II
Only P-SAA with no chirality and no hierarchy: Example I

Figure 6-1. General overview of the identification of the hierarchy and chirality of self-assembled aggregates (**SAA**) of a given self-assembly building unit (**SA-BU**). **AP** is asymmetric packing segment. **SA** and **P-SAA** refer to self-assembly and primary self-assembled aggregate, respectively.

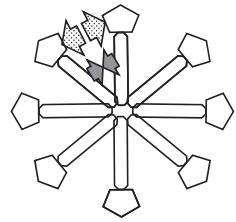
of possessing a morphological chirality. Its overall morphology will be likely asymmetric. The same follow-up question should be asked. It is whether the building unit has the capability of multi-step self-assembly. If the answer is no, there will be only primary aggregates formed from this building unit. And they will show a morphological chirality unless the environmental condition works against it. But it will have no hierarchy. This is *example III*. If the answer is yes, there will be higher-order aggregates, and they will have a strong possibility of showing both hierarchy and chirality. This is *example IV*.

For many self-assembly systems, directional segments do not significantly affect the expression of morphological chirality. As will be shown in the next sections, this independence of directional segments from asymmetric packing segments makes the application of the segmental analysis more versatile.

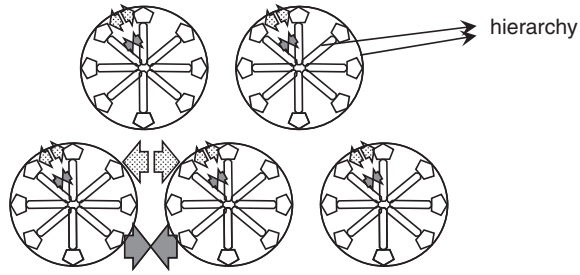
6.3. ASSEMBLY PRINCIPLES

Figure 6-2 shows the schematic representations for the identification of the hierarchy and chirality of self-assembled aggregates. The symbols representing each segment come from Figures 1-3 and 1-5. To be consistent, all of the schematic illustrations are taken from Figures 5-3 and 5-7. The numbering with capital letters parallels that in Figure 6-1. These are designed for molecular primary aggregates. However, they work fine for most colloidal building units as well.

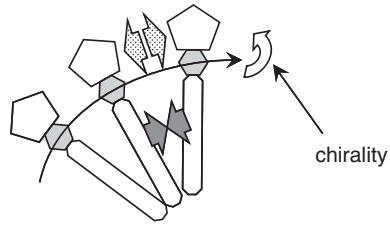
I. **P-SAA** with no hierarchy and no chirality



II. Higher-order **SAA**s with hierarchy but without chirality



III. **P-SAA** with chirality but no hierarchy



IV. Higher-order **SAA**s with hierarchy and chirality

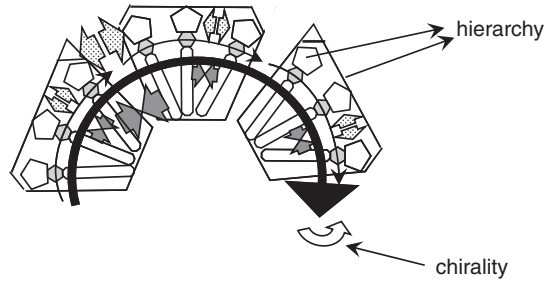


Figure 6-2. Schematic explanation of the identification of the hierarchy and chirality of self-assembled aggregates (**SAA**). **P-SAA** is short for primary self-assembled aggregate.

A review by Smith (2009) shows the direct translation of the chiral information of molecular building units into nanoscale aggregates during hierarchical self-assembly. Induction, memory, and amplification of molecular chirality during heterogeneous hierarchical self-assembly are also shown using porphyrin-based building units (Rosaria et al., 2008). An article by Praveen et al. (2008) competently reviews how the attachment of the chiral motif (asymmetric packing segment) on linear π-conjugated building units changes the structures of the helical aggregates and their hierarchical networks.

6.3.1. Molecular Systems

The first example in the figure is the building unit without an asymmetric packing segment and without the capability of multi-step self-assembly. It thus inevitably forms a symmetric morphology of primary aggregates. There will be no higher-order aggregates. No asymmetric packing segments within the primary building units means that there will be no chirality for the primary aggregates. In addition, the symmetric morphology suggests that there will be no morphological chirality, either. It is assumed here that the experimental condition is only to promote self-assembly, and the external force is assumed to be none. Hence, it is not possible that the morphological chirality is generated by non-intrinsic (other than structural) factors. No formation of higher-order aggregates simply means that there will be no hierarchy, either. The second example is the primary building unit without an asymmetric packing segment but with the capability of multi-step self-assembly. It thus has a strong possibility of forming higher-order aggregates. Whenever this becomes the case, it is possible for them to express hierarchy. But they will show no clear chirality. It would be a safe prediction that as the self-assembly continues into higher orders, a higher degree of hierarchy can be obtained. Shown in the figure is the hierarchy in the secondary aggregates, which means the hierarchy that consists of the primary and secondary building units.

The third example has now an asymmetric packing segment within the primary building unit. But it does not have a capability of multi-step self-assembly. Thereby, it forms only primary aggregates. No multi-step self-assembly almost always means that there will be no hierarchy. The asymmetric packing segment, however, is an intrinsic one. It will be preserved in (or transferred into) the primary aggregates. But the chirality that we describe here is not the intrinsic chirality. It is a morphological chirality that is induced by the intrinsic factor. Again, if it is assumed that no other conditional and external force factors work against the action of the asymmetric packing segments, the primary aggregates have no choice but to express morphological chirality. The last example is the same building unit but with the capability of multi-step self-assembly. The intrinsic chirality of the primary building unit will be preserved throughout multi-step self-assembly. Under the same conditional assumption of no extrinsic intervention, the same will hold for morphological chirality. The morphological chirality that is generated during the primary self-assembly will be transferred into the secondary aggregates, which in turn will be transferred into the tertiary aggregates, if there are any. As the self-assembly continues into higher-orders, the morphological chirality also acquires its

own hierarchy. This might be called *hierarchical chirality*. This concept is very useful when applied to some important issues of nanotechnology systems. As is true for the hierarchy, the logic is the same as in the second example. The secondary aggregates have dual hierarchy that consists of the primary and secondary building units, and the tertiary aggregates would have triple hierarchy that is composed of the primary, secondary, and tertiary building units.

Let us now explore how this schematic explanation can be applied to actual self-assembly building units. Figure 6-3 shows how the hierarchy and chirality of the self-assembled aggregates of molecular and bio-mimetic building units can be predicted with a reasonable accuracy. For the first two examples, cationic surfactant, dodecyltrimethylammonium bromide, is used. A zwitterionic lipid, 1,2-dipalmitoyl-*L*-α-phosphatidylcholine, is chosen for the second two examples. Their molecular structures and segmental structures were shown in Figure 5-4. The self-assembly condition is assumed to be in water at room temperature. It is also assumed that the condition for the higher-order self-assemblies for examples II and IV is the increase of their concentrations. The concentrations for examples I and III are for the primary self-assembly only.

The first example is when dodecyltrimethylammonium bromide molecules form a spherical micelle with a well-defined *cmc* (critical micellar concentration). Its segmental structure shows no asymmetric packing segment, and its concentration is assumed to have no capability of multi-step self-assembly. A spherical micelle

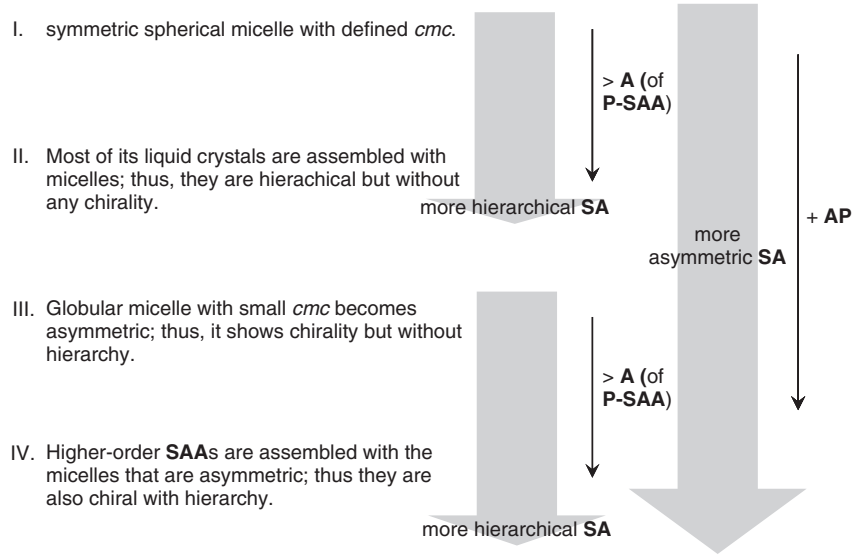

I. symmetric spherical micelle with defined *cmc*.
II. Most of its liquid crystals are assembled with micelles; thus, they are hierachical but without any chirality.
III. Globular micelle with small *cmc* becomes asymmetric; thus, it shows chirality but without hierarchy.
IV. Higher-order **SAA**s are assembled with the micelles that are asymmetric; thus they are also chiral with hierarchy.
> **A** (of **P-SAA**)
more hierarchical **SA**
more asymmetric **SA**
+ **AP**
> **A** (of **P-SAA**)
more hierarchical **SA**

Figure 6-3. Prediction of the hierarchy and chirality of self-assembled aggregates (**SAA**) of different molecular and bio-mimetic self-assembly building units based on the segmental analysis: in water at room temperature. **A** and **AP** refer to attractive and asymmetric packing segments, respectively. **SA** and **P-SAA** are short for self-assembly and primary self-assembled aggregate, respectively. *cmc* is critical micellar concentration.

that is symmetric means that there is no chirality. And no self-assembly between the micelles means that there is no hierarchy, either. However, when the concentration is increased to the point where the secondary self-assembly can be favored, the liquid crystals begin to form. Most of the liquid crystals are assembled from micelles. Thus, they have hierarchy. But still there is no reason for this liquid crystal to obtain chirality. For these first two examples, the general trend is relatively simple to state. As the attractive segment of the primary aggregates (micelles) is increased (as the concentration of the primary building units [dodecyltrimethylammonium bromides] is increased), the self-assembly becomes more hierarchical. Chirality is not affected by this change in the segmental structure. There is simply no asymmetrical packing segment within the building units.

For the third example, 1,2-dipalmitoyl-*L*-α-phosphatidylcholine has one chiral carbon, which is its asymmetric packing segment. The details are shown in Figure 5-4. When the self-assembly takes place only for the primary step, it is more likely that there will be the formation of globular micelles (primary aggregates) with a very small value of *cmc*. It is also very likely that the asymmetric packing segment induces morphological chirality, which will be expressed by the asymmetric overall morphology of the micelles. It does show chirality. But the concentration is still low so that only the primary aggregates exist. Therefore, there will be no hierarchy. The last example is the same one with a concentration that is now high enough to have the secondary self-assembly. Basically, the segmental analysis reveals that the formation of the secondary aggregates is a result of the self-assembly of the primary aggregates. The asymmetric nature of the primary aggregates from example III is highly likely to be preserved within the secondary aggregates, and at the same time it is strongly possible that the asymmetric nature acts to give the secondary aggregates an asymmetric overall morphology. This means that the secondary aggregates in this example have chirality. Also, the multistep self-assembly means that they obtain hierarchy as well. For examples III and IV, the general trend is the same as for examples I and II. As the attractive segment of the primary aggregates is increased (as a result of the increasing concentration of the primary building units), the self-assembly becomes more hierarchical while the chirality is transferred into higher-order aggregates.

Generally speaking, when asymmetric packing segments are involved, the self-assembly becomes more asymmetric, which, in most cases, results in the formation of morphological chirality. This is not limited only to the relatively simple building units like those shown in this figure. As long as a segmental analysis is performed clearly, and it shows that there is at least one asymmetric packing segment, it should be safe to assume that the self-assembly takes place in an asymmetric manner. For some building units that have a long chainlike structure, such as polymer chains or proteins, the formation of a helix can be explained in a purely entropic manner (Snir and Kamien, 2005). This implies that the asymmetric packing segment is not the only factor that can induce an asymmetric self-assembly. An asymmetric self-assembly can often be induced without the asymmetric packing segments. In this regard and also with the notion of force balance for the formation of morphological chirality, it will be very intuitive to refer to the article that demonstrates that the

origin of helical nanostructures should be attributed to the competition between surface free energy reduction and torsion strain energy increase (Zhao et al., 2009).

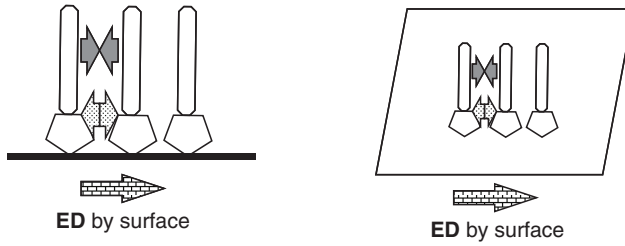
6.3.2. Surface Systems

This subsection shows how the concept of segmental analysis can be applied to the self-assembly at surfaces. Both solid- and liquid-based surfaces will be described. The general outline of the discussion might be somewhat different from that of self-assembly in bulk solutions. However, it shows that the application of the segmental analysis to self-assembly issues is basically the same both at surfaces and in solutions. For surface self-assembly, it is the factors that might be induced by the surfaces that should be considered as additional segments.

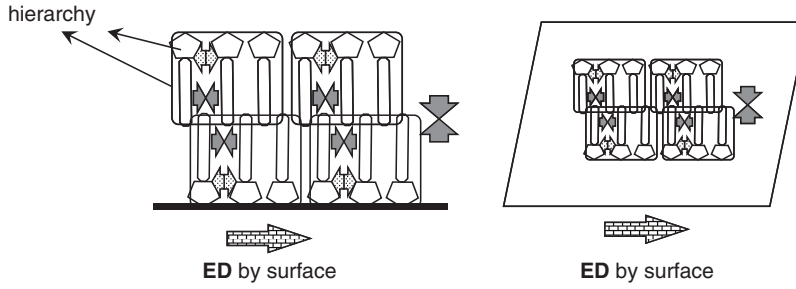
Figure 6-4 shows the schematic explanation of the identification of the hierarchy and chirality of surface self-assembled aggregates. For surface self-assembly, the building units can assemble in either upright or lying-down (or flat) packing mode on surfaces. Figure 3-9 showed more details for this. The schematic illustrations in Figure 6-4 are effective for both packing modes. For all four examples, the schemes on the left-hand side represent the upright packing mode while those at the right-hand side are for the lying-down mode. For the schematic illustrations in Figure 6-2, a directional segment was not included. All of the examples in this figure have a directional factor that is induced by surface. The symbols representing each segment are from Figures 1-3 and 1-5.

The first example is a molecular building unit that has the attractive and repulsive segments only. The difference from example I of Figure 6-2 is that the system now has an external force–induced directional factor (for details, refer to Subsection 1.2.2.2) that is a result of the interaction of the building unit with surface. Since there is no difference made for a directional segment in Figure 6-1, this corresponds to example I in the flowchart. The force balance between the attractive and repulsive segments will be symmetric just like the one in bulk. But the directional factor will direct the self-assembly along the direction of surface. It is also assumed that the self-assembly is favored only up to the primary step by conditional factors such as the concentration of building units and the size (available surface area) of the surface. Then, the most probable outcome should be a monolayer type of primary self-assembled aggregates. There cannot be chirality because there is no asymmetric packing segment within the primary building unit. Since the assembly is limited only up to the primary, there will be no hierarchy, either. For the second example, it is assumed that the concentration of building units or the size of surface allows the building units to continue into the higher-order self-assembly. For surface self-assembly, the general route for the secondary self-assembly is somewhat different from the one in bulk even with exactly the same building units. For the self-assembly in bulk, it causes no significant trouble to predict the outcome of the secondary self-assembly by analyzing it to be a force balance between the primary aggregates. For the surface self-assembly, on the other hand, the secondary self-assembly is rather close to the succession of another primary assembly on top of the primary aggregates. It usually is not easy to picture the force balance between

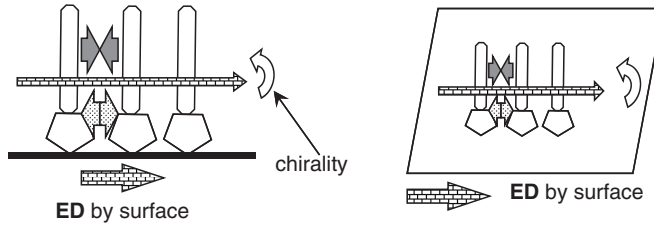
I. Surface **P-SAA** with no hierarchy and no chirality.



II. Surface higher-order **SAA**s with hierarchy but without chirality.



III. Surface **P-SAA** with chirality but no hierarchy.



IV. Surface higher-order **SAA**s with hierarchy and chirality.

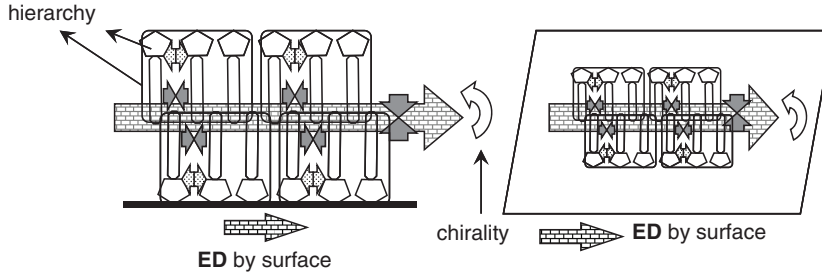


Figure 6-4. Schematic explanation of the identification of the hierarchy and chirality of surface self-assembled aggregates (**SAA**). **P-SAA** is short for primary self-assembled aggregate. **ED** is external force–induced directional factor.

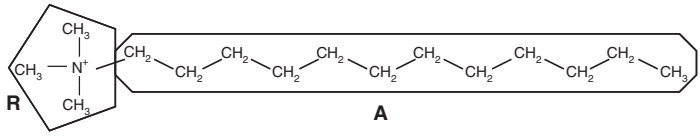
the surface self-assembled aggregates. The primary aggregates are simply only on the surface. However, because of this unique geometrical constraint of surface self-assembly, the overall morphology of the aggregates formed during the secondary assembly has, in most cases, no choice but to show the multilayer type of structure. This can be viewed as a result of the interaction between the primary aggregates that are monolayer because the results will be the same for either of the processes. The schematic illustration in the figure is designed to show this aspect. Thus, the same sense of hierarchy as for bulk self-assembled aggregates can be given to this surface self-assembled aggregate. Shown is the dual hierarchy that is composed of the primary and secondary building units. It still has no chirality because the building unit has no asymmetric packing segment.

Before we go for the third and fourth examples, let us assume that, for these two, the asymmetric packing of the primary building unit is induced by surface. More precisely, the force balance between the primary building units and the surface is achieved in a way that it breaks the symmetry of the primary building units. Hence, the chirality here is induced by the surface-induced asymmetric packing of the primary building units. For this reason, the asymmetric packing segments are not present within the primary building units. For the third example, the segmental structure and conditional factor are the same as for example I except that there is now surface-induced asymmetric packing factor. A result of this segmental structure is the primary aggregates, which should be a monolayer type with chirality. An explicit condition for no higher-order self-assembly means that there will be no hierarchy. For the last example, it is now assumed that the conditional factors allow the primary building units to assemble beyond the primary step. With the same logic as in example II, this secondary self-assembly can be viewed as the interaction between the primary aggregates, thereby as the self-assembly between the primary aggregates. The morphological chirality of the primary aggregates that was the result of the interaction with the surface induces the morphological asymmetric feature to the higher-order aggregates. This means that the surface higher-order aggregates possess morphological chirality. The capability of multi-step self-assembly, with the same logic as above, means that the secondary aggregates have a hierarchical feature as well. As in example II, it is the dual hierarchy that is composed of the primary and secondary building units.

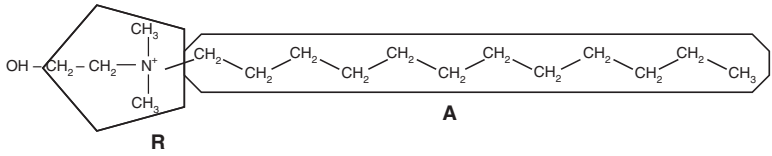
Figure 6-5 shows the prediction of the hierarchy and chirality of surface self-assembled aggregates based on the structures of the primary building units. Two different molecular building units are used here. Figure 6-5(a) shows their segmental analyses. For cases I and II, dodecyltrimethylammonium bromide is used. For cases III and IV, the same molecule, but with one of the methyl groups at the head group replaced with 2-hydroxyethyl moiety, is used for the primary building unit. These two building units have been shown in Figure 5-4. However, the directional segment in Figure 5-4 for the second building unit, which was the hydroxyl group, is not assigned here for surface self-assembly. While the hydroxyl group in Figure 5-4 was a typical directional segment due to its hydrogen-bonding capability, for the surface self-assembly here it is assumed that the self-assembly condition allows the hydroxyl groups to mainly interact with surface.

(a) Structures of **SA-BU**s and surface

For cases I and II:



For cases III and IV:



charged (or hydroxylated) silica solid

(b) Prediction

I. symmetric semimicelle with defined surface *cmc*

II. Bilayer, trilayer, or multilayer; thus, with hierarchy but without any chirality

III. Mainly monolayer form with asymmetric packing; thus, with chirality but no hierarchy

IV A strong possibility of bilayer, trilayer, or multilayer types of **SAA**s that are asymmetric; thus, with chirality and hierarchy

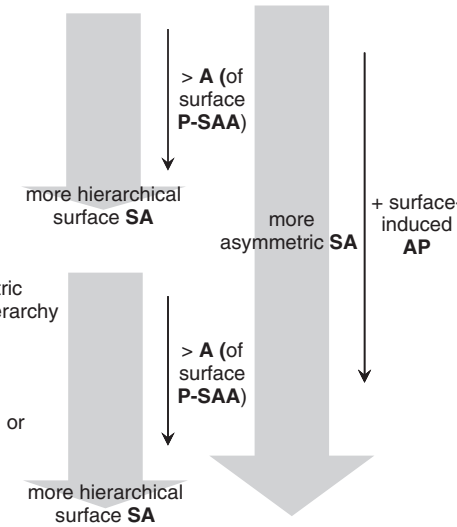

> A (of surface P-SAA)
more hierarchical surface SA
more asymmetric SA
+ surface-induced AP
> A (of surface P-SAA)
more hierarchical surface SA

Figure 6-5. Prediction of the hierarchy and chirality of surface self-assembled aggregates (**SAA**) of different molecular self-assembly building units (**SA-BU**) on solid surface based on the segmental analysis. **A, R**, and **AP** refer to attractive, repulsive, and asymmetric packing segments, respectively. **SA** and **P-SAA** are short for self-assembly and primary self-assembled aggregate, respectively. *cmc* is critical micellar concentration.

The surface here is silica solid. And its surface is assumed to be charged or hydroxylated. The condition is in water at room temperature. For both building units, the dodecyl hydrocarbon chain is their attractive segment because of its capability of attractive hydrophobic interaction between them. This should be a valid assignment as long as the surface self-assembly occurs with the configuration that its initial interaction is between the ionic head groups and the surface. This allows the dodecyl chains to be away from the surface, hence gives them enough degrees of freedom to interact each other. The charged or hydroxylated silica surface satisfies this self-assembly configuration with both building units. For the repulsive segment, the head groups with positively charged nitrogen atom are the only candidates for both building units. And this assignment requires some additional analysis in terms of their interaction mode, which is different from the one in bulk. For their self-assembly in bulk solution, it was the electrostatic repulsive force that originated from the head group that counterbalanced the attractive hydrophobic force between the hydrocarbon chains. Thus, they had a classic type of repulsive segment. However, when their initial self-assembly occurs on the surface of silica, the positively charged nitrogen atoms are primarily interacting with the charges on the silica surface through the electrostatic attractive interaction. Therefore, it is the bulkiness of their head groups that can induce the steric repulsion after their binding on the surface of silica.

Compared with the electrostatic interaction, this steric repulsion on the surface of silica might not be a prominent one. But it will have some degree of impact on the packing density (or coverage) of the head groups, which provides enough rationale to have them assigned as a repulsive segment even for the primary self-assembly. For the higher-order self-assembly, these nitrogen atom-based head groups will be free from interaction with the surface of silica. They can interact through the electrostatic repulsive interaction just like for the self-assembly in bulk, which causes them to be assigned as a repulsive segment.

The general trend of the hierarchy and chirality of the surface self-assembled aggregates of the two building units is described in Figure 6-5(b). As is true for those in Figure 6-3, the self-assembly conditions for examples I and III are limited only to the primary assembly. Also, the higher-order aggregates are assumed to be formed by the increased concentration of the primary building units on a defined area of the silica surface. It may be also possible through a successive self-assembly. But the outcome can be viewed as the same as a result of the higher-order assembly. For purpose of explanation only, in examples III and IV it is assumed that, as a result of the interaction of the head group (the hydroxyl group) with the silica surface, there is a symmetry breaking in the primary building unit. This is again only for purpose of explanation; it may not be the case for many similar systems. It may take a very precise setting of a condition to have this realized, or it may need a primary building unit that has a functional group with a stronger affinity with the silica surface. An example is dicarboxylic acid–based long hydrocarbons. However, by accepting the assumption of the symmetry breaking for these two examples, the general tendency for their chirality can be understood more easily,

which will eventually help us understand more complicated surface self-assembly systems in a systematic manner.

For the first example, the self-assembly of dodecyltrimethylammonium molecules on the silica surface will result in the formation of semimicelle. It will have a relatively well-defined value of surface *cmc*. Semimicelle usually has a good possibility of having some degree of distortion due to the interaction with surface. However, it is still symmetric along the axis that runs through the direction of surface and along the axis that is vertical to surface. Thus, no chirality can be formed. And no higher-order self-assemblies means no hierarchy. The second example is the same self-assembly system but with the capability of the higher-order self-assembly. This is when the primary aggregates have a conditional attractive segment. Depending on the degree of the higher-order self-assembly, bilayer, trilayer, and multilayer types of higher-order aggregates can be formed, which means that they obtain a morphological hierarchy. Since there are no factors that can induce an asymmetric packing, the possibility of expressing a morphological chirality is negligible.

Case Study 6.1

Amphiphilic alkyloligosiloxane homologue series self-assembled on the surface of rubbing-treated polyimide substrate (Du et al., 2009). These particular self-assembly building units have an attractive segment only. The example from the literature that was presented for Figure 3-9 (Case Study 3.5) has more about this segmental analysis, and Figure 11.2(a) explains the logic behind it. The initial interaction of the building units with the surface occurs through the hydrophobic attraction between the alkyl chains of the building units and the alkyl moieties of the surface. This resulted in a self-assembly with a lying-down packing mode. If the concentrations of the building units were kept low, monolayer morphology of hemimicelles (for the one with decyl chain) or low-coverage of lamellar structures (for the one with hexadecyl chain) would have been formed with defined surface *cmc*s, which would make a good actual example for case I with a lying-down mode. Since their films were prepared by dip-coating of the sol followed by drying, it can be easily predicted that the concentrations of the building units kept increasing to the point where only hydrated forms of the aggregates were left. This experimental condition guarantees to provide the conditional attractive segment for the primary aggregates. The results indeed show the formation of multilayer types of higher-order aggregates of hexagonal (for the one with decyl chain) and lamellar (for the one with hexadecyl chain) structures, which means that they acquired morphological hierarchy. It makes a good example for case II.

For the third example, the self-assembly was limited only to the primary assembly. But the primary building units assemble on the silica surface through an asymmetric packing as a result of the symmetry breaking. The outcome thus will be mainly the monolayer type of primary aggregates with a morphological chirality. For the same reason as in the first example, there will be no morphological hierarchy. For the last example, the self-assembly condition favors the

higher-order self-assembly even though the first layer of interaction occurs with a symmetry breaking. Once the first layer of the aggregates expresses an asymmetric packing morphology, it is highly likely that the following order of self-assembly occurs based on this morphological asymmetric nature; thus the possibility that the higher-order aggregates have a morphological chirality is high. The fact that they can have not only monolayer but bilayer and multilayer types of structures as well indicates that they have a morphological hierarchy.

Case Study 6.2

It was shown that stereochemical properties play a critical role in determining the orders within the self-assembled structures for the formation of methylthiolate self-assembled monolayers on gold surface (Voznyy et al., 2009). The inherent chirality of the low coverage phase governs the structural evolution at higher coverage. This result provides a real example for an asymmetric surface self-assembly that is induced by surface-induced asymmetric packing segment, which can be nicely correlated with the understanding of the example from the literature (Bierman et al., 2008) that is cited for the surface nanoassembly for the third example in Figure 11-6 (Case Study 11.1).

Case Study 6.3

There is another important report, regarding the discussion here, which shows that sodium dodecylsulfate forms self-assembled aggregates on the surface of carbon nanotubes with interesting asymmetric characteristics including helices and double helices. It is upright mode assembly. Furthermore, the formation of this morphological chirality is dependent on the surface symmetry of the carbon nanotubes (Richard et al., 2003). Depending on the detailed structures of the carbon nanotubes, this symmetry can be broken, which can be analyzed as the asymmetric packing segment of the nanotubes. Thus, this result can be viewed as the case where the asymmetric packing segment of the surface directly induces the chiral self-assembly of the building unit that does not possess any asymmetric packing segment.

Case Study 6.4

Morphological chirality of surface self-assembled aggregates can also be induced by the asymmetric packing segment of building unit. This is well demonstrated by the study that shows the formation of spiral-shaped aggregates on the surface of a single-walled carbon nanotube (Wu et al., 2006). The building unit used for this study is 1-palmitoyl-3-glyceryl phosphorylcholine, which is a typical single-chain phospholipid. As with 1,2-dipalmitoyl-*L*-α-phosphatidylcholine in Figure 5-4, it has one chiral carbon that should be assigned as its asymmetric packing segment.

Case Study 6.5

For a comprehensive collection of surface hierarchical self-assemblies that take place in lying-down packing mode, please refer to Yang and Wang (2009). The elemental building unit and the building block (or secondary building block) in their scheme correspond to the primary self-assembly building unit and the secondary self-assembly building unit (primary self-assembled aggregate) in this book, respectively. This work provides plenty of actual examples for all four cases having lying-down mode in Figure 6-4, and nicely demonstrates the fact that the balance between the intermolecular interactions (between the building units and with surface) is crucial for the understanding of their self-assemblies. An additional attractive segment for the higher-order self-assemblies is often provided by the increased concentrations of the primary building units. It also shows that whether the symmetric breaking of the building unit is induced by the surface or the building unit has its own chirality (this is the asymmetric packing segment), the morphological chirality of the aggregates is clearly expressed through the higher-order self-assemblies. For many, it occurs up to the secondary self-assembly. And for some, it occurs up to the tertiary self-assembly.

Case Study 6.6

There is a beautiful experimental report (Écija et al., 2010) that clearly demonstrates the hierarchical chiral surface self-assembly. Their building unit is a porphyrin derivative that has a conformational flexibility. This is an achiral molecule in nature, but because of this conformational flexibility, when it assembles on the surface of silver, the molecular chirality is induced by the molecular distortion. This is the asymmetric packing segment of this assembly system. Because of the size of this building unit, it has van der Waals attractive force, and this is its attractive segment. Steric repulsion caused by the side chains is its repulsive segment. The directionality of this self-assembly is mainly provided by the silver surface, in other words, by the surface-induced directional factor. A weak hydrogen bonding certainly contributes to this directionality to some degree, thus making a directional segment. The shape of this building unit, which is somewhat slender, could make some degree of contribution to the directionality of the assembly as well, though this is not resolved.

What is fascinating about this report is that it presents beautiful STM images that clearly show not only the multi-step (up to tertiary) self-assemblies and their three levels of hierarchy, but the chirality of each level of assembled aggregates and their transfer through the multi-step assemblies as well. The porphyrin derivative is the primary self-assembly building unit of this assembly system. The trimer of this primary building unit (called *secondary supramolecular unit*) is the primary self-assembled aggregate, and shows a clear aggregation number, which is three. This trimer is the secondary self-assembly building unit as well. Three trimers assemble into larger aggregates. This is the

secondary self-assembled aggregate with again a clear aggregation number of three and it makes the tertiary self-assembly building unit. The tertiary building units finally assemble into the homochiral nanoporous networks, which is the tertiary self-assembled aggregate of their assembly system. These results are remarkable considering the fact that this is a surface self-assembly and surface self-assemblies usually do not reveal their aggregation numbers and hierarchies that easily. Furthermore, this assembly system clearly proves that the chiroselective self-assembly can be designed on surfaces, which could have many interesting application possibilities. This assembly system belongs to example IV of Figures 6-1 and 6-4.

The overall trend now looks almost the same as the one in Figure 6-3. More hierarchical surface self-assemblies take place as the attractive segments of the primary surface self-assembled aggregates are increased. And as the surface-induced asymmetric packing segments are increased, more chiral self-assemblies are induced on the surface. The same segmental analysis is effective whether the aggregates are formed in bulk solutions or on surfaces.

6.4. COLLECTION OF HIERARCHY WITHIN SELF-ASSEMBLED AGGREGATES

Table 6-1 lists the collection of common morphological hierarchy expressed by self-assembled aggregates. Hierarchy of aggregates can appear only on higher-order aggregates. Thus, the aggregates that are relevant for these hierarchical structures are those from Tables 4-1 and 4-2. Whenever one of these structures is mentioned in the literature, it is almost certainly a result of multi-step self-assembly. One thing to remember while referring to this table is that, as the structural order of aggregates is increased, so is their delicate dependency on conditional factors. This is why the external force–induced directional factor is crucial for the formation of many hierarchical structures. It is not unusual to see dramatic changes in hierarchical structures even when the experimental condition is changed slightly. For example, micelle liquid crystal structures can experience diverse changes depending on the concentrations of their building units or solvents. For details on external force–induced directional factor, see Subsection 1.2.2.2. Usually, the hierarchical structures of biological aggregates are relatively stable for a wider range of environmental conditions. For them, the directional segments take on a more important role than the external force–induced directional factor.

As discussed throughout this chapter, while it is possible to predict whether the aggregate would have hierarchy and what the most likely overall morphology would be, it is not easy to predict the exact structures of hierarchy. There are simply too many varieties. But by cross-referencing this table with Tables 4-1, 4-2, and 5-2, it is possible to correlate what type of building unit would self-assemble into which structure of higher-order aggregate, and what type of hierarchical structure would likely be obtained. For example, Table 4-1 says that any surfactant

TABLE 6-1. Collection of common hierarchy within the higher-order self-assembled aggregates that are shown in Tables 4-1 and 4-2, and the segment combination of the building units with which each structure is most likely formed. D and AP refer to directional and asymmetric packing segments, respectively. ED is external force–induced directional factor.

Hierarchical Structure	Segment Combination of Building Unit
liquid crystals built from micelles	any combination with **ED**
multiple sheets built on monolayers	any combination with **ED**
nanoparticle-in-nanoshell	any combination with **ED**
nanoparticle chain-in-nanofiber	any combination with **ED**
nanocomposites (most of them)	any combination with **ED**
vesicle-in-nanotube	any combination with **ED**
vesicle-in-vesicle	any combination with **ED**
fullerene-in-carbon nanotube	any combination with **ED**
nanoribbon (non-chiral)[a]	with **D** and **ED**
concentric circular	with **D** and **ED**
folded helical chain	with **D** and **AP**
networked helical chain	with **D** and **AP**
bundled helical chain	with **D** and **AP**
fibril-in-fibril	with **D** and **AP**

[a]Usually hetero-aggregates formed on surface by inclusion of discrete defects.

building unit with attractive and repulsive segments can multi-self-assemble into surfactant mesophase. And Table 5-2 says that this high-order aggregate has a crystal-like structure. Then, Table 6-1 says that this liquid crystal structure along with its building unit (micelle) makes its hierarchy. This type of correlation between basic building units and morphological characteristics can make the design and fabrication of nanotechnology systems very systematic. For many, those hierarchical structures of higher-order aggregates can be directly copied within nanostructures, which in turn can offer many interesting nanoproperties. The orders of the aggregates become the structural orders of the nanostructures. Overall structures usually reach microscale and often go beyond it, but the sizes of the primary structural orders almost always remain within the nanometer range. Chapters 11 and 12 have more detailed analysis of this relationship between self-assembled aggregates and nanostructures and eventually with nanoproperties.

6.5. COLLECTION OF CHIRALITY EXPRESSED BY SELF-ASSEMBLED AGGREGATES

Table 6-2 lists the collection of common morphological chirality expressed by self-assembled aggregates. Chirality can appear on aggregates with any structural orders. Thus, the aggregates that are relevant for these chiral structures are all of those from Tables 3-1, 4-1, and 4-2. Whenever one of these structures is referred to for aggregates in the literature, it almost certainly has morphological chirality. In terms of segmental analysis, the presence of asymmetric packing segment is crucial for the expression of chirality. In almost all cases, the self-assembly building units

TABLE 6-2. Collection of common chirality within the self-assembled aggregates that are shown in Tables 3-1, 4-1, and 4-2, and the segment combination of the building units with which each structure is most likely formed. D and AP refer to directional and asymmetric packing segments, respectively. ED is external force–induced directional factor.

Chiral Structure	Segment Combination of Building Unit
helical tube	with **AP** or **ED**
helical chain	with **AP** or **ED**
spiral	with **AP** or **ED**
coil	with **AP** or **ED**
symmetry-broken layer	with **AP** or **ED**
nanoribbon (chiral)[a]	multiple **D** and **AP**
β-sheet	with **AP** or **ED**
double helix	with **AP**

[a]Usually hetero-aggregates formed in solution by continuous structural distortion, and has hierarchy as well.

should have at least one asymmetric packing segment, or they should have multiple directional segments whose interaction with each other can generate asymmetric assembly of the building units. Often, purely environmental factors can generate the asymmetric packing, too. Existence of asymmetric packing segments or factors does not necessarily mean that there will be morphological chirality. Sometimes, it is canceled out by other segments such as strong repulsive or attractive segments. Many of the chiralities have biological origin, which means that either they are from biological systems or they are expressed by the aggregates of biological or bio-mimetic building units.

Hierarchy and chirality of the self-assembled aggregates are independent of each other. Presence of hierarchy for a certain aggregate does not mean that it has chirality, and vice versa. The prediction of chirality using segmental analysis is somewhat easier than for hierarchy. The structural varieties are not as diverse as those of hierarchy. And the chirality parameters such as pitch size and its periodicity can be reasonably controlled by using the general trend of their changes once a well-studied reference chiral system is in hand. Also, by cross-referencing this table with Tables 3-1, 4-1, 4-2, 5-1, and 5-2, it is possible to correlate what type of building unit would self-assemble into what structure of aggregate, and what type of chirality can be anticipated from it. For example, Table 4-1 says that elongated threadlike micelles can be assembled from polymeric, biological, or bio-mimetic building units that have directional and asymmetric packing segments. And Table 5-2 says that this aggregate has fibrous structure. Then, Table 6-2 says that its likely chirality would be the nanoribbon type.

Along with the hierarchy from the above subsection, this type of structure–property relationship can make the design and fabrication of nanotechnology systems quite systematic. For many systems, those chiral structures of aggregates can be directly copied within nanostructures, which in turn can offer many interesting nanoproperties such as chirooptical effects. Chapters 11 and 12 have more details on the impact of hierarchy and chirality of aggregates on the generation

of many distinctive nanostructures and subsequent nanoproperties. Particularly for the chirality of aggregates, its unique assembly processes including self-assembly, self-assembly–disassembly, and self-assembly–disassembly–reassembly, can offer very important insights for the design of the operating nanoscale parts, thereby for nanomechanics. Biological systems have already mastered this aspect for many of their vital operations. Both will be examined more deeply in Chapter 14.

6.6. SUMMARY

This chapter discussed how the two important morphological characteristics of self-assembled aggregates, hierarchy and chirality, can be studied in a systematic manner. It showed that:

1. The structural analysis of self-assembly building units (segmental analysis) offers a facile means to identify the hierarchy and chirality of the aggregates with any structural orders.
2. The capability of multi-step self-assembly is critical for the expression of hierarchy.
3. An asymmetric packing of building units that is provided by asymmetric packing segments or certain external factors is the key to the expression of chirality.
4. It is effective for self-assemblies both in bulk solutions and at surfaces.

One specific issue that was discussed in the previous chapter was the unclear distinction between different orders of self-assemblies. This becomes an important issue for the hierarchy and chirality of aggregates as well. It may hinder the exact nature of hierarchy. It may also yield complications, especially for surface self-assembled aggregates. The exact degree of hierarchy usually will not need to be resolved. But it often becomes necessary structural information for its incorporation into some nanotechnology systems. The same goes for chirality. Proper addressing of this issue is important to expand its applicability for structurally unclear but practical aggregates.

Another issue is related to the analysis of asymmetric packing segments. Under a certain condition, the building units with a clear asymmetric packing segment can be forced to form symmetric overall morphology. It could be induced either by nearly complete morphological counterbalance within the aggregates or by symmetric packing between the building units forced by a specific external force. This is an important aspect to explore because it often provides unexpected novel properties. However, this vanishing asymmetric packing segment may make the segmental analysis complicated. Certainly, more systematic studies for different conditional factors are needed. This might be achieved by developing *reverse segmental analysis*. First, set up an assembly guideline for conditional factors by using well-studied building units, and use it as a reference. Then, analyze the conditional factors and building units under study as if they were derived from those of the reference.

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7

Assembly with Multiple Building Units

7.1. ASSEMBLY ISSUE

There are four fundamental pillars in the nanoscale signatures that cover almost all of the nanotechnology systems. They are nanoscale *pore*, nanoscale *film*, nanoscale *particle*, and nanoscale *device/machine*. To make the advance of nanotechnology more practical and, more importantly, human- and eco-friendly, the assembly of these nanoscale signatures should be effective and efficient. This goal can become realistic by applying the principles and practicality of self-assembly for nanotechnology systems.

In the past, we sometimes rushed into the commercialization of newly discovered materials without proper assessment of their hazardous properties. Their detrimental side effects were often found later or at the end of their life cycles, which forced us to scramble to clean them up from our environment. It took a lot of effort and high costs, but in many cases the damage already had been done. Nanotechnology is basically about the interesting and novel physical, chemical, optical, and spectroscopic properties that are being discovered in the nanoscale. But it would be too naïve to assume that all those properties are advantageous for us and benign to our environment. Nanotechnology *can* and *should* be "green." The first step toward this goal is to develop effective tools that can be readily applied for the assembly of nanotechnology systems so that they can make the development of nanotechnology systems purpose oriented and streamlined. Discovering novel properties from them will follow. For more discussions about green nanoscience and green nanotechnology and their relations with the principles of green chemistry, please see Dahl et al.

Self-Assembly and Nanotechnology Systems: Design, Characterization, and Applications, First Edition. Yoon S. Lee.
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(2007) and Hutchison (2008). They also discuss the importance and implication of self-assembly on green nanoscience and green nanotechnology.

Some nanotechnology systems are composed of a small number of simple building units, which makes their assembly straightforward. However, there are many other nanotechnology systems that are composed of a large number of different types of building units. Their assembly still can be relatively straightforward, but they usually need properly designed assembly routes or improved assembly power. This and the next few chapters discuss these issues. This chapter describes the design of proper assembly routes and the next chapter shows how to improve the assembility and directionality of the designed assembly routes. The different types of building units here include self-assembly, fabrication, and reactive building units. They often include substrates, too. Self-assembly building units along with fabrication and reactive building units make nanoassembly building units. (See Section 2.2 for the details. Section 1.5 presents the collection of self-assembly building units. And Section 2.7 has the collection of nanoassembly building units.) Thus, the *assembly* in this and next few chapters refers to the *nanoassembly* (for the details, see Section 2.1). By the definition shown in Section 2.6, the assembled systems of nanoassembly building units are nanoassembled systems. Nanoassembled systems include self-assembled aggregates and are a part of nanotechnology systems.

Assembly routes for nanoassembled systems can be divided into two distinctive types: *homogeneous* and *heterogeneous*. Simply stated, a homogeneous route is an assembly that deals with one type of nanoassembly building unit. A heterogeneous route has multiple types of building units. The design of nanoassembled systems can be made efficient and practical by selecting the proper route at the beginning of the assembly process. In addition, it could minimize unnecessary trial-and-error steps. The issue that will be addressed in this chapter is:

How can the most effective assembly route be determined for a given set of nanoassembly building units?

This issue is further specified as follows:

When will a homogeneous route be enough?

When should a heterogeneous route be applied?

How can an assembly route be effectively adjusted for a specific nanoelement?

If it is decided that a homogeneous route is more practical for given building units, their assembly can be straightforward. It can be very much like a single step of self-assembly. If, however, a heterogeneous route is found to be more practical, their assembly becomes complicated. It requires a detailed analysis of the assembly process to meet with the force balance condition. It could be a single step. But it will be most likely either multi-step or even hierarchical. This will be very much like a multi-step self-assembly that expresses hierarchy and chirality.

7.2. GENERAL OVERVIEW

Figure 7-1 shows a general overview for the determination of the assembly route for given nanoassembly building units. The first step is the identification of the nature of the nanoassembled system to be developed. This will lead to identifying proper building units for it. This first step can be reversed. In many cases, building units can be given first, and the nanoassembled system has to be assembled to express the intended nature. This step also has to clarify the types of building units. There are three different types of building units: self-assembly, fabrication, and reactive building units. If only one type of building unit is required, the assembly can take a much simpler homogeneous route. Whether the building units are composed of only one kind (i.e., only atomic, molecular, or colloidal) or multiple kinds (i.e., molecular with colloidal, atomic with colloidal, and so forth), as long as they belong to one type, it is a single type of assembly system.

The homogeneous route can be very straightforward. For most cases, a one-step process (or one-pot) with all-at-once mode can complete the assembly (for more about the different assembly routes and modes, see Figure 2-1). Successive assembly, which means repeating the same process until the nanoassembled system is obtained, can be practical, too. This is *case I* for the next few sections. If multiple types of building units are identified for a certain assembly system, it is more likely

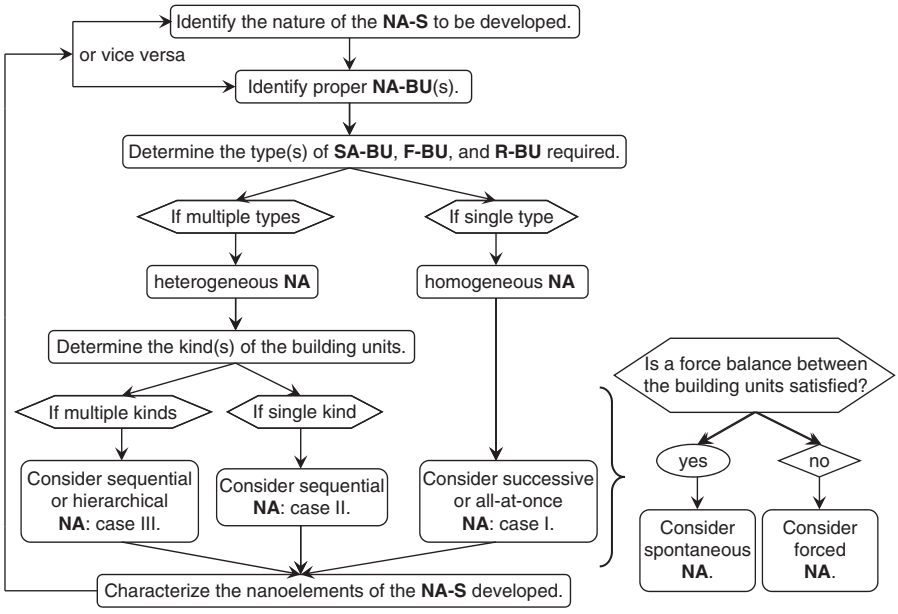

Identify the nature of the NA-S to be developed.
or vice versa
Identify proper NA-BU(s).
Determine the type(s) of SA-BU, F-BU, and R-BU required.
If multiple types
If single type
heterogeneous NA
homogeneous NA
Determine the kind(s) of the building units.
If multiple kinds
If single kind
Consider sequential or hierarchical NA: case III.
Consider sequential NA: case II.
Consider successive or all-at-once NA: case I.
Is a force balance between the building units satisfied?
yes
no
Consider spontaneous NA.
Consider forced NA.
Characterize the nanoelements of the NA-S developed.

Figure 7-1. General overview for the design of assembly with multiple building units. **NA, NA-BU**, and **NA-S** are short for nanoassembly, nanoassembly building unit, and nanoassembled system, respectively. **SA-BU, F-BU**, and **R-BU** refer to self-assembly, fabrication, and reactive building units, respectively.

that the assembly has to take a couple of different steps. This is a heterogeneous route. The next step is to determine the kinds of building units. This means whether the building units have the same kind of nature or not. For example, if all of the different types of building units are molecular ones or all of them are colloidal ones, they are the same kinds. On the other hand, if the building units have, for example, a fabrication building unit having molecular nature and a reactive building unit having atomic nature, or a fabrication building unit having molecular nature and a self-assembly building unit having colloidal nature, they have multiple kinds of building units. When an assembly system has a single kind of building units, it is a sequential assembly that can be more practical. This is *case II*. If it has multiple kinds, a sequential assembly with hierarchical character would be the most effective. This is *case III*. Whatever assembly route is chosen, once a nanoassembled system is obtained, its nanoelement (for the details, see Section 2.3) has to be characterized. If the nanoelement does not satisfy the requirement that was set at the beginning, the whole process may have to be repeated. It may require a different nature of the nanoassembled system or different building units. Another option is taking the nanoelement as a new one and searching for proper places to apply it.

A separate diagram on the right-hand side of the figure is to address whether the assembly route from the main diagram can satisfy the force balance between the building units. If so, the assembly can be spontaneous. If not, the only way to achieve the assembly is to use external forces unless it is more practical to have different building units or modify the selected building units. This will be the main topic for the next chapter.

7.3. ASSEMBLY PRINCIPLES

This section shows detailed principles of different assembly routes. Examples and their general assembly trends will be followed. For more details about the structural analysis of building units (*segmental analysis*), see Subsection 1.2.2.

7.3.1. Analysis of Building Units

Figure 7-2 shows nanoassembly building units. The symbols representing each type of building units come from Figure 2-1. For each kind of building units, rectangular and circular shapes of symbols are used for molecular and colloidal building units, respectively. A biological building unit is considered as a molecular one. A polymer building unit is represented as a linear chain, which is just for brevity.

Figure 7-2(a) has self-assembly building units. Dodecyltrimethylammonium bromide was repeatedly used in the previous chapters. It is one of the typical cationic surfactants, and has one attractive segment (hydrocarbon chain) and one repulsive segment (trimethylammonium head group). For details, see Figure 3-2. The next one is polystyrene colloidal particle with natural surface charges. This is a typical colloidal building unit, and has attractive and repulsive segments. Figures 3-5 and

3-6 give the details for this analysis. The third building unit is polyelectrolyte. Poly(ethyleneimine) is a linear type of polyelectrolyte. Its capability of hydrophobic attraction between hydrocarbon chains can be assigned as its attractive segment, and its ionic nature, which is dependent on solution pH, can give it a repulsive segment. Thus, this polyelectrolyte has both attractive and repulsive segments.

The last one has a biological origin. Collagen is a linear rod–type of aggregate that is composed of helically twisted protein chains. Three amino acids make this protein chain: glycine, proline, and hydroxyproline. The first two are standard amino acids while the third one is nonstandard. The length of its long axis is ~300 nm and its diameter is 1.5 nm. More detailed physical and biological properties will not be discussed here. However, as far as segmental analysis is concerned, collagen has an important aspect that finds a good practicality for many nanoassembly

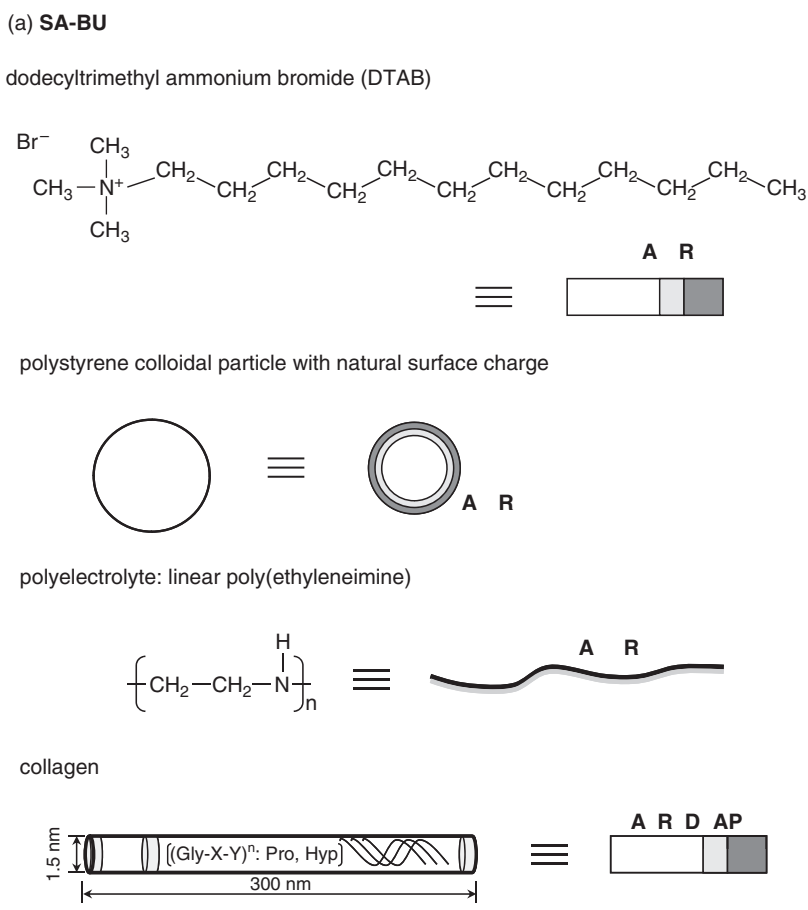
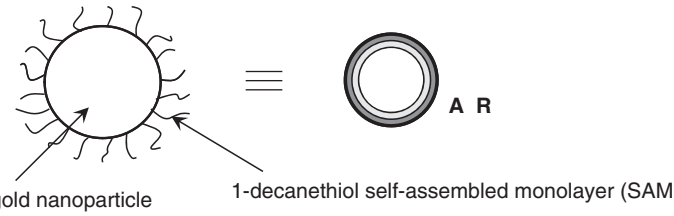


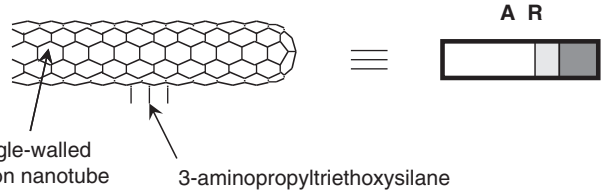
Figure 7-2. Building units. **SA-BU, F-BU**, and **R-BU** refer to self-assembly, fabrication, and reactive building units, respectively. **A, R, D**, and **AP** refer to attractive, repulsive, directional, and asymmetric packing segments, respectively.

(b) **F-BU**

decanethiol-protected gold nanoparticle

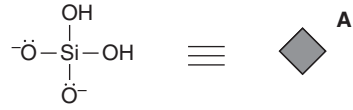


surface silylated carbon nanotube

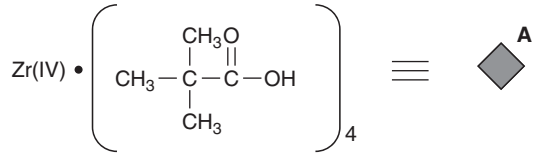


(c) **R-BU**

silicate anion



2,2-dimethyl propanoic acid, zirconium(4+) salt



gold vapor

Figure 7-2. (*Continued*)

processes. It first has attractive and repulsive segments. But unlike typical molecular building units such as dodecyltrimethylammonium bromide, they do not come from a specific part of the molecule. And unlike the typical colloidal building unit, such as polystyrene particle, they do not come from the physical nature of colloid, either. The attractive segment of collagen is a result of an intricate combination

of molecular parts that induce an attractive force with its colloidal nature that generates van der Waals force.

Similarly, the repulsive segment of collagen is a combination of molecular parts that induce a repulsive force at the surface with the surface charges that originate from the nature of its component. All three amino acids of collagen have directional and asymmetric packing segments, which, by the way, are the source of its characteristic physical and biological properties. Both of them are expressed on the surface of collagen, not just buried inside of it. Hence, it can be concluded that collagen has not only the attractive and repulsive segments but also the directional and asymmetric packing segments as well. If only its size matters, collagen can be considered as a colloidal building unit rather than a biological one.

Figure 7-2(b) shows fabrication building units. Fabrication building units are those that two or more self-assembly building units have assembled into one building unit. There are numerous nanoparticles (or colloidal particles) that are used as a fabrication building unit. In most cases, to achieve a force balance, the surfaces of these nanoparticles have to be properly modified. The first building unit in the figure is a typical example. The gold nanoparticle whose surface is modified (protected or decorated) with decanethiol can have clearly defined attractive and repulsive segments. Without this modification, the gold surface cannot produce enough steric effect, which will result in a lack of repulsive force. The modification is performed through a somewhat unconventional self-assembly that is involved with a thiol–gold bonding. The result of this assembly is called a *self-assembled monolayer (SAM)*. The second building unit is a carbon nanotube whose surface is modified through a surface silylation. The details about carbon nanotube are beyond the scope of this book. However, it is now obvious that carbon nanotube is one of the most important nanoassembly building units. For many cases, carbon nanotube can be directly put into nanoassembly processes. (If this should be the case, the carbon nanotube is a self-assembly building unit for that specific nanoassembly instead of a fabrication building unit.) This is especially true when external force is used for the nanoassembly. Given the nature of pristine carbon nanotube, it can be determined that it has a clear attractive segment but not a significant repulsive segment. But, for many other cases, to become a part of nanoassembly, carbon nanotube should have a clear repulsive segment. This is usually achieved through modification of its surface with the proper molecule. These modifying molecules are those that can generate the repulsive force from the surface of carbon nanotube. It is mostly through steric or electrostatic force. Shown in Figure 7-2(b) is a single-walled carbon nanotube whose surface is modified with 3-aminopropyltriethoxysilane. This gives the nanotube a clear repulsive segment, which is an electrostatic repulsive interaction induced by the amine groups (at proper solution pH) located at the foremost area of the surface. The van der Waals attractive force is its attractive segment.

Figure 7-2(c) shows reactive building units. Reactive building units are those that have a reactive part. They can be composed of any one of or any possible combination of the fundamental and additional segments just like self-assembly and fabrication building units. However, they usually assembled as a form having

only one attractive segment, which is the reactive part itself. This can make the force balance less complicated. Otherwise, it is more likely that the segmental structure of reactive building units varies constantly as their reaction occurs during nanoassembly. The first one is silicate anion. This may be the most often used reactive building unit for nanoassembly. Its unique physicochemical properties and easy-to-process character are certainly the most important reasons for its popularity. The degree of its protonation or deprotonation is strongly dependent on solution pH. But regardless of the actual form participating in nanoassembly, all four side-groups will be a part of the reaction. Even though it is somewhat different from other attractive interactions where the action is induced by nonreactive interaction, this also can be viewed as an attractive interaction in the sense that it brings the building units together. Silicate anion is thus a reactive building unit that has one attractive segment.

The same interpretation can be applied to the other two building units. 2,2-dimethyl propanoic acid, zirconium(4+) salt has a bulky part other than zirconium ion. This bulky part is important to stabilize the entire salt so that it can safely deliver the building unit to the right place during nanoassembly. But this bulky part is not participated into the actual assembly. It is the zirconium ion that assembles through reduction and thus forms a zirconium-based system. Hence, this salt is a reactive building unit with one attractive segment. The third one is gold vapor. Metal vapors are also a popular nanoassembly building unit. Creation of nanostructures through different types of vapor depositions is a good example of their use. Usually, they collide onto target surfaces as a form of atomic beam and form a structure that is intended. It thus should be viewed as a reactive building unit that has one attractive segment.

7.3.2. Assembly of Nanoassembled Systems

Representative examples of each of the three cases from Figure 7-1 are described with details in this section. The building units are limited to those introduced in the previous subsection.

7.3.2.1. Homogeneous Assemblies. Figure 7-3 shows four examples of the assembly of nanoassembled systems through the homogeneous route. This makes them belong to case I of Figure 7-1. The first two are for the all-at-once mode, and the remaining two are for the successive mode. For all examples, the purpose of the nanoassembled system is indicated. This is arbitrary but makes the discussion more realistic.

The first example is homogeneous, all-at-once nanoassembly. Let us assume that the purpose is to have a photonic band gap device. Figure 7-3(a) shows the schematic illustration. The photonic band gap is one of the typical phenomena that are induced by the particles having a colloidal length scale. They also have to be assembled into clearly defined colloidal crystals with a minimum number of structural defects. Obviously, the building units should be something with a colloidal size. We have a polystyrene particle in Figure 7-2 that has attractive

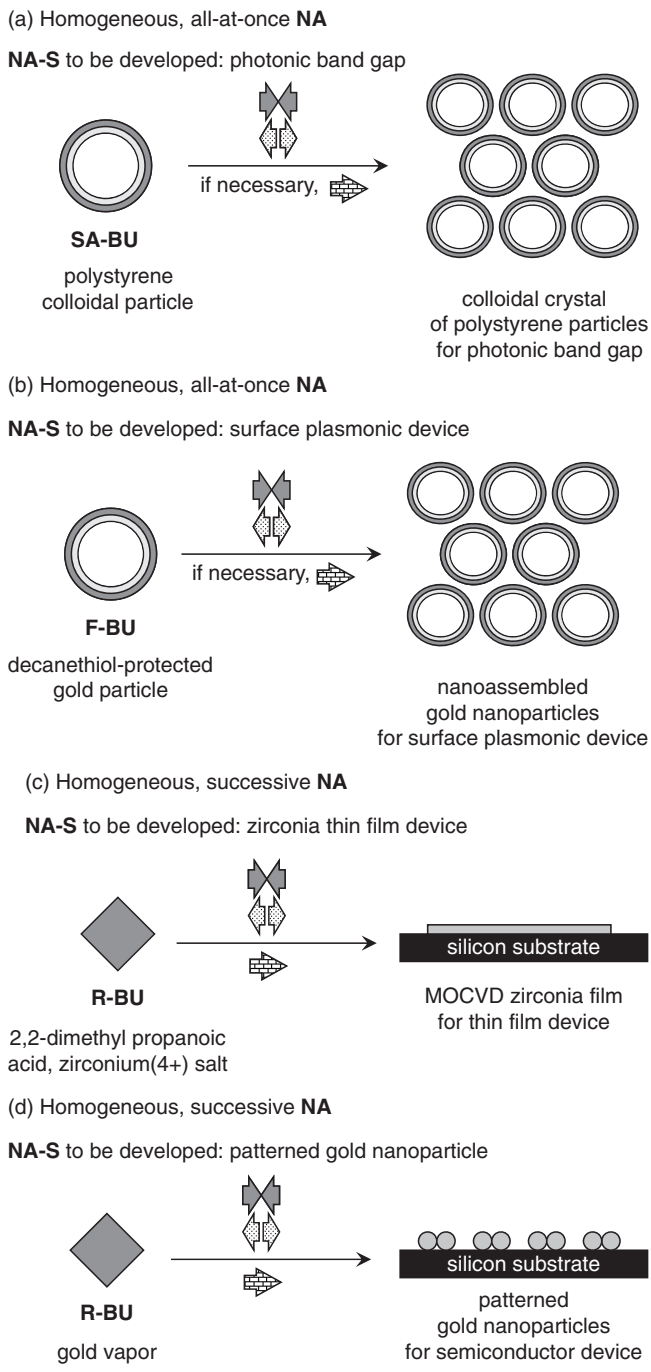


Figure 7-3. Assembly of nanoassembled systems (**NA-S**): case I. **NA** is short for nanoassembly. **SA-BU, F-BU**, and **R-BU** refer to self-assembly, fabrication, and reactive building units, respectively.

and repulsive segments. No other building units are necessary since all it takes is to assemble the particles into a well-organized colloidal crystal. It makes this assembly system a single type of assembly. Its relatively simple segmental structure tells us that once the solution condition is properly given, the particles should assemble into a stable aggregate through their own force balance. There is no need of additional agents to assist this force balance, and no need of external forces, either. Therefore, it should have little difficulty coming up with a colloidal crystal through the homogeneous route with one step (all-at-once) of assembly. The main nanoelement to be characterized is whether the colloidal crystal shows the photonic band gap. If it does not show a proper property, the diagram in Figure 7-1 advises us to go back to the first step. The nature of this particular nanoassembled system is clear; thus it would be a good option to consider revising the building unit. Possibly, by changing the size of the particle, a better expression of nanoproperty could be achieved.

The second example is an assembly of a surface plasmonic device. Figure 7-3(b) shows the schematic illustration. The surface plasmon property is a unique optical property that is generated by certain metals whose sizes are in the nanometer range. Hence, among the building units in Figure 7-2, the gold nanoparticle is the only one that can express the surface plasmon phenomenon. For its proper expression as a form of device, the gold nanoparticles should be assembled as a certain size of aggregate. They are modified with decanethiol self-assembled monolayer, which gives them attractive and repulsive segments. It thus requires only one type of building unit, which makes this a single type of assembly. In addition, this segmental structure strongly implies that it should assemble homogeneously in solution through the force balance between its own segments. Single step (all-at-once) process is enough to achieve this assembly. The nanoassembled gold nanoparticles should then be characterized to see whether they show a surface plasmonic property. If this nanoelement is not satisfactory, the process should go back to the first step. Employing different sizes of gold nanoparticles and/or using alkanethiol with different hydrocarbon chain lengths, which changes the distance between the gold nanoparticles once they are assembled, would be the most practical options.

The third example is a homogeneous assembly with successive mode. It is assumed that zirconia thin film device is a nanoassembled system to be developed. Figure 7-3(c) is the schematic illustration. One building unit in Figure 7-2, 2,2-dimethyl propanoic acid, zirconium(4+) salt, can be used for this. This makes this assembly system the one with a single type of reactive building unit. Films can be assembled only with an assist of proper substrates. Silicon solid is chosen as a substrate for this assembly system. It is arbitrary and not intended to express any specific meaning. As much freedom as possible can be exercised in the selection of substrate, which is dependent on many factors, including the reactivity of the solid with incoming reactive building units, the degree of participation of the solid substrate as a part of the device function, the structure on the solid surface that is desirable for the creation of nanoscale structure on zirconia film, and so forth. The zirconium salt has only one segment, which is attractive. Once it colloids with the silicon surface as a form of molecular beam, it will keep depositing either

until the molecular beam runs out or until there is no more available space on the silicon surface, unless the beam is targeted on a specific region on the silicon surface by allowing a vertical growth of zirconium. Whatever the case, this is a homogeneous route and the molecular beam should be deposited with a successive mode to guarantee the formation of thin film. The silicon surface is the source of the directional force that makes zirconium a film. The repulsive force that counterbalances the attractive force during the assembly is conditional. This particular type of assembly has a well-known name, *metal-organic chemical vapor deposition (MOCVD)*, which is widely used for the formation of thin film by using different types of reactive building units. The main nanoelement to be inspected is a nanostructural element. One possible adjustment, when it is not satisfactory, is a zirconium precursor with a different organic part, which could cause zirconium ion to be deposited with a different charge. A different charge here in turn means a different degree of attractive segment.

Figure 7-3(d) is the last example. The nanoassembled system to be assembled is patterned gold nanoparticles on the surface of solid substrate. Both the gold nanoparticle whose surface is decorated with decanethiol self-assembled monolayer and the gold vapor can be a building unit for this purpose. But for this example, it is assumed to assemble a semiconductor device so that its surface should be able to conduct surface electrons and holes. The gold nanoparticle would certainly satisfy this requirement. However, it requires a post-assembly treatment in order to remove the decanethiol molecules from the gold nanoparticles so that the bare gold surface is exposed. The gold vapor, on the other hand, would not need this additional step, which therefore makes it a more logical choice. To work as a semiconductor device, gold should be assembled on a specific solid substrate. Silicon is selected for this. As with the third example, this is an arbitrary choice. There can be plenty of other options for substrates depending on the purpose. A key difference from the third example in terms of silicon substrate is the presence of pre-patterns. For the previous example, the silicon surface is assumed to be atomically flat or have a roughness at least a degree less than the thickness of the zirconium film, which was to meet the purpose of the assembled system that was a smooth thin film. For the example here, it is assumed that the surface of the silicon substrate is pre-patterned so that it can have a structural inhomogeneity at the nanometer scale. This is to ensure regularly patterned specific sites on the surface of silicon where the gold vapor can have a more favorable assembly tendency so that the formation of the gold nanoparticles can be achieved in a patterned way as well. This spatial constraint on surface (it could be called *surface constraint* as well, depending on how it is viewed) will act as a repulsive segment during the assembly. One building unit here means that this is a single type.

The diagram in Figure 7-1 tells us that the homogeneous assembly is a proper route to take. The reactive gold vapor, once it is beamed on the surface of silicon, has no other option but to be deposited on the specific sites where it has more favorability. This is a homogeneous process. And it has to continue to the level where the formation of nanoparticles with the desired size and pattern is achieved. Therefore, it has to be a successive assembly. The attractive segment of

the gold vapor is the driving force for this assembly. The silicon surface acts as a directional segment that guides the direction of the patterning. Nanostructural element is certainly the primary nanoelement to be characterized in order to confirm whether the nanoassembled system has the structural features required to ensure the semiconductive property. The nanoproperty element that actually confirms the semiconductive property should be tracked. The nature of the gold nanoassembled system is the subject to be adjusted here. Hence, if nanoelements are not satisfactorily achieved, it would be a good exercise to change the condition for the beaming of the gold vapor. This can adjust or optimize the attractive interaction of the gold vapor with the surface of silicon.

7.3.2.2. Sequential Assemblies. This subsection shows the assembly of nanoassembled systems through a heterogeneous route with sequential mode. This is for case II and some of case III in Figure 7-1. Figure 7-4 is the schematic illustration. As with the previous homogeneous assembly, a nanoassembled system to be developed is assumed for each example.

The first example is shown in Figure 7-4(a). This is to develop a binary colloidal crystal for optical device. There certainly can be many different choices for the colloidal building units for this purpose. But Figure 7-2 introduced two distinctive colloidal building units: polystyrene self-assembly building unit and decanethiol-protected gold nanoparticle fabrication building unit. And judging by their sizes and physical properties, these two can be excellent building units for the assembly of colloidal crystal–based optical devices. We thus have two different types of building units, and the diagram in Figure 7-1 says that a heterogeneous route can be a better option for their effective assembly. Also, both of them happen to be a colloid. Thus, they are the same kind of building units.

The diagram in Figure 7-1 again says that a sequential mode under the heterogeneous route can be a better choice. Let us assume here that the size of polystyrene is much bigger than that of gold nanoparticle. Then, the assembly can be more effective by starting with the assembly of bigger building units. Polystyrene has clear attractive and repulsive segments. This should allow them to self-assemble once they are placed in a proper solution. Unless this should occur under an unusual situation, there is no need of external force. This first step should produce a colloidal crystal of polystyrene particles with a satisfactory overall size and quality. The quality here is mainly related to the degree of the structural defects and overall integrity. A sequential mode means repeating the same (or similar) process but with different building units. For this assembly system, it means repeating with gold building units and the polystyrene colloidal crystal. Gold nanoparticles have their own attractive and repulsive segments. Once they are placed in a proper solution with the polystyrene colloidal crystal, which is assumed here to have a good structural integrity and enough interstitial regions where smaller gold nanoparticles can fit in, the gold nanoparticles now face a strong directional force induced by the colloidal crystal. This is a directional force that acts on the gold nanoparticles and confines them within the interstitial regions. It has mainly a capillary force origin. Once located inside, the force balance between their attractive and repulsive segments will play out to regularly arrange them. This sequential assembly can ensure

that the binary colloidal crystal assembled is truly a binary one, which means that the two building units are evenly dispersed at the length scale of their own sizes. A binary colloidal crystal should not mean a colloidal crystal having two separate regions in each building unit. Overall, by combining this second step with the first one, it is a heterogeneous assembly. In certain cases, if the structural condition is

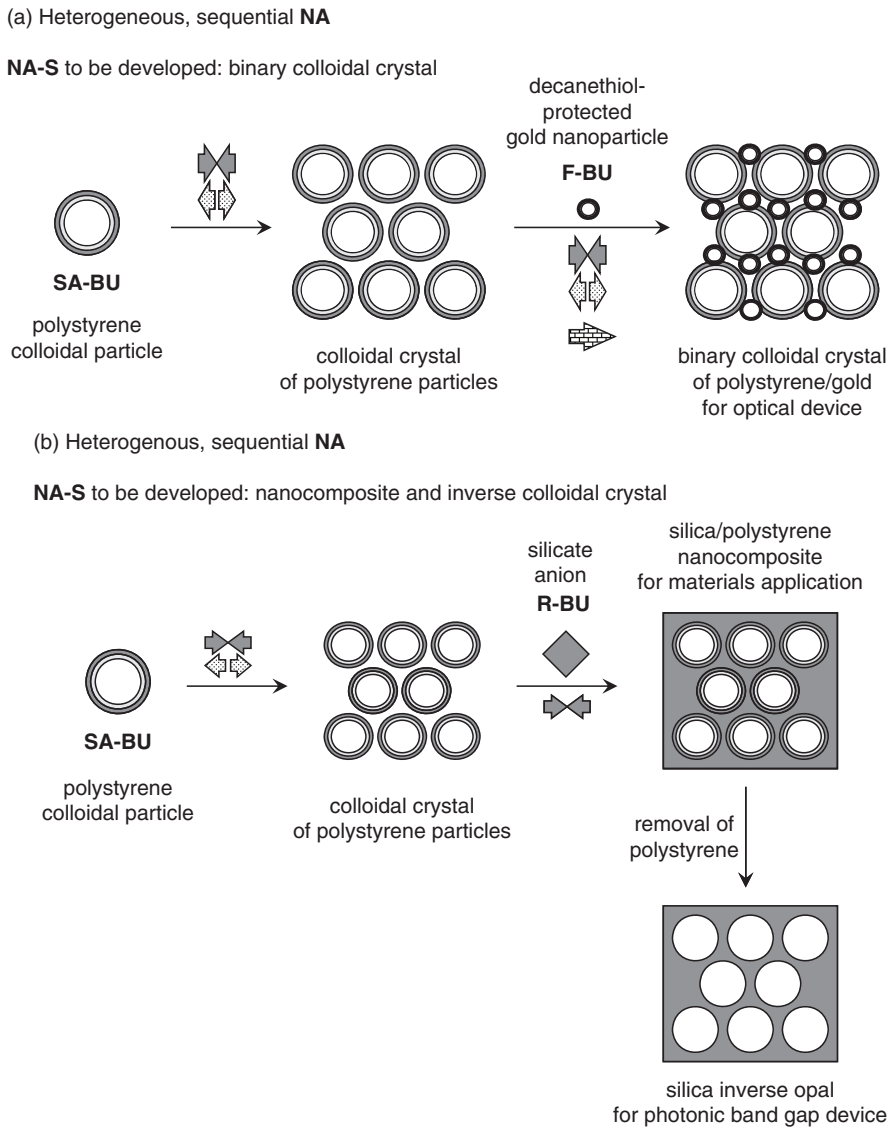

(a) Heterogeneous, sequential **NA**
NA-S to be developed: binary colloidal crystal
decanethiol-protected gold nanoparticle
F-BU
SA-BU
polystyrene colloidal particle
colloidal crystal of polystyrene particles
binary colloidal crystal of polystyrene/gold for optical device
(b) Heterogenous, sequential **NA**
NA-S to be developed: nanocomposite and inverse colloidal crystal
silicate anion
R-BU
silica/polystyrene nanocomposite for materials application
SA-BU
polystyrene colloidal particle
colloidal crystal of polystyrene particles
removal of polystyrene
silica inverse opal for photonic band gap device

Figure 7-4. Assembly of nanoassembled systems (**NA-S**): case II and sequential nanoassembly (**NA**) of case III. **SA-BU, F-BU**, and **R-BU** refer to self-assembly, fabrication, and reactive building units, respectively.

(c) Heterogeneous, sequential **NA**

NA-S to be developed: nanoparticle/polymer nanocomposite

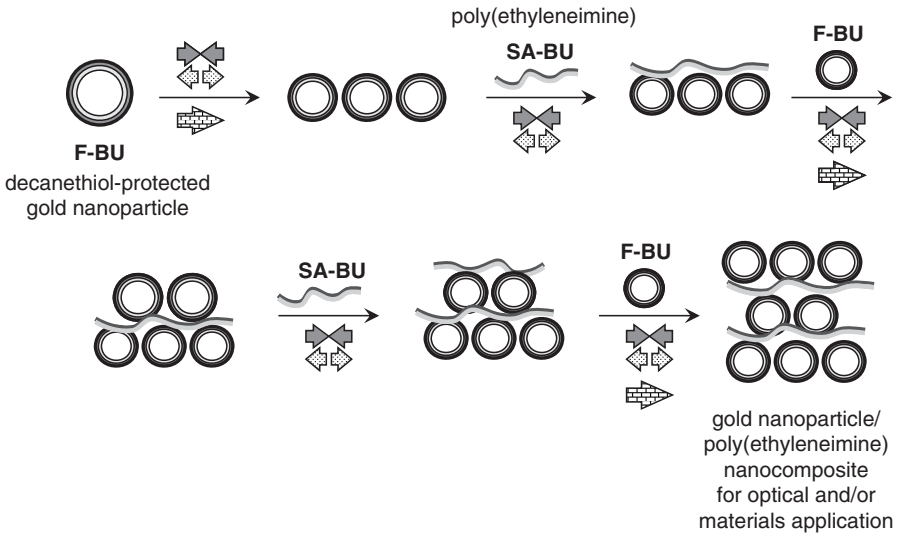


Figure 7-4. (*Continued*)

ideal, there is the possibility that a homogeneous all-at-once assembly will form the binary colloidal crystal.

The diagram in Figure 7-1 can also offer derived routes and modes. The nanoelements to be characterized should be nanoproperty and nanostructural ones in order to make sure that proper optical properties are expressed from the right nanostructures. Changes in the size ratios between the polystyrene and gold building units can provide practical room to tune the nanoelements. Some related arguments for the formation of binary nanoparticle superlattices and the role of underlying forces have been reported (Talapin, 2008).

The second example is shown in Figure 7-4(b). It is to have a nanocomposite and inverse colloidal crystal that can be useful for a reinforced material and photonic band gap device, respectively. Two different building units have to be selected for this purpose. The first one should be a colloidal building unit to ensure the assembly of colloidal crystal, and the second one should be something that can create the nanocomposite with the colloidal crystal. Polystyrene colloidal building unit and silicate anion reactive building unit are ideal among those in Figure 7-2. These are two different types of building units, which guides us to consider a heterogeneous route. Also, they have a colloidal and molecular nature, respectively, which means that they are two different kinds of building units. Hence, this assembly system belongs to case III in Figure 7-1. This says that a sequential or hierarchical assembly mode would be effective. But given the purpose, a sequential mode will be more practical. The assembly of polystyrene colloidal crystal is the same as for the

first step of the previous example in Figure 7-4(a). The next step is to assemble this colloidal crystal with silicate anions. Silicate anion has only one attractive segment. Thus, once it is placed with the polystyrene colloidal crystal under a proper condition, it will be attracted both inside and outside of the colloidal crystal and condense into silica. The result is silica/polystyrene nanocomposite. This is a typical sol-gel reaction. By carefully manipulating the size of the polystyrene particle and the degree of the silica condensation, this nanocomposite can find good use in a diverse range of materials applications. For this nanocomposite, the primary nanoelements to be characterized are nanostructural and nanoproperty elements, which ensures the right material property can be generated from the right structural feature.

A similar process was repeated with two different types of building units, which makes the overall assembly a sequential one. The next step to obtain the inverse colloidal crystal can be achieved through doing a simple hydrothermal treatment to the silica/polystyrene nanocomposite. Silica has much higher thermal stability than polystyrene so that this treatment removes the polystyrene part from the nanocomposite and leaves the silica part only. The silica part retains the structural features that are coined by the polystyrene particles. This is a silica inverse opal, and it can be very useful as a photonic band gap device. Nanoproperty element should be carefully examined to ensure the proper band gap property. Nanostructural characterization should be also performed whenever it is relevant to ensure the right nanoproperty for this nanoassembled system.

Case Study 7.1

The formation of silica and zinc sulfide nanohelices by metal-driven self-assembly (Qiao et al., 2009) offers a close experimental example. They used two distinctive nanoassembly building units. Sodium cholate is their self-assembly building unit while precursors for silica and zinc sulfide are reactive building units. All of them have a molecular nature. Thus, this nanoassembly system has two different types of building unit in a single kind. Figure 7-1 says that a heterogeneous route with a sequential mode would be the most effective option. They indeed followed this path. The soft nanohelices of the self-assembly building unit were assembled first, which was followed by the addition of proper reactive building units. This is again through a sequential nanoassembly, not a hierarchical one. The hierarchy and chirality of the nanohelices were obtained due to the nature of the self-assembly building unit, which possesses asymmetric packing segments and the capability of multi-step self-assembly.

The third example is shown in Figure 7-4(c). This is to obtain a nanoparticle/polymer nanocomposite. Metal nanoparticles regularly embedded within polymer matrix often show interesting synergistic properties, which can be useful for optical devices and materials application. Figure 7-2 has gold nanoparticle. In addition, poly(ethyleneimine) building unit should be added to this nanoassembly system. As a typical ionic polyelectrolyte, its linear chain can make the force balance with gold nanoparticle more practical. Two different types of building

units are now chosen. They are one fabrication building unit and one self-assembly building unit, which make this system favorable for a heterogeneous route. Furthermore, gold nanoparticle has a colloidal nature while poly(ethyleneimine) is a polymer. Thus, this system has two different kinds of building units. Hence, as with the second example, this system also belongs to case III in Figure 7-1, and either a sequential or a hierarchical mode would be proper to choose.

However, given the purpose, it will be more practical to choose a sequential mode. The first step is to assemble gold nanoparticles into a colloidal film. This needs assistance from solid substrate. For brevity, the substrate is not included. The gold nanoparticles protected with decanethiol self-assembled monolayers have their own attractive and repulsive segments. They are balanced during this initial step. A substrate provides a directional force. A sequential mode repeats a similar assembly with different building units. The poly(ethyleneimine) chain has its own attractive and repulsive segments, too. As long as the condition is right, the attractive segment from gold nanoparticle interacts with the attractive segment from poly(ethyleneimine). As this attractive process takes place, the repulsive segments from both building units counterbalance it until the two forces are balanced. This second step assembles the first layer of nanoparticle/polymer composite. The number of layers of the polymer on top of the nanoparticle array can be controlled by controlling the amount of poly(ethyleneimine).

The third step is to assemble another layer of gold nanoparticles on top of this first layer of nanoparticle/polymer composite. The same attractive and repulsive segments work exactly the same way as for the assembly of the first layer. This generates the second layer of gold nanoparticles. Whether taking another step in this sequential process is optional depends on the requirements of the nanoassembled system. For this, it is hard to imagine that the nanoparticle/polymer nanocomposite can be obtained through the all-at-once or successive mode. Nanoproperty and nanostructural elements have to be examined to confirm the optical and/or materials properties that have to come from the right nanostructure. If necessary, adjustment can be made by changing the size of gold nanoparticle and by modifying the attractive and repulsive segments of poly(ethyleneimine).

Case Study 7.2

An experimental study that reports the assembly of PEG(polyethylene glycol)-modified nanogel (Oishi et al., 2009) is an actual case that is close to this third example. Oishi et al. used three building units: methacrylate-based polymer particle having acetal groups and PEG chains on its surface, chloroauric acid as the precursor of gold nanoparticle, and sodium salt of 1,3,6,8-pyrenetetrasulfonic acid, which is an ionic dye. The first one is a colloidal fabrication building unit since it has modified surface. The second one is a reactive building unit, and the third one is a self-assembly building unit. Both the second and third ones have a molecular nature. This makes this assembly system have three building

units of different types and kinds. Figure 7-1 leads us to take a heterogeneous route with either sequential or hierarchical mode. Given the purpose of the nanoassembled system, which is a functional release of dye molecules from the nanogel, hierarchy of the nanogel would be an unnecessary structural feature, and it is not quite possible, either, due to the nature of the building units. The sequential mode is the one that can ensure an effective assembly. They took three steps of assembly: assembly of polymer particles as gel, assembly of gold nanoparticles within the interstitial regions of the gel, and assembly of dye molecules with the gold nanoparticle–embedded gel. This is a typical sequential assembly since it is a repeat of a similar process with different building units. Successive assembly cannot be an option here. And if all-at-once assembly had been used, the nanoassembled system would have ended up with poorly developed gold nanoparticle, poorly developed gel state, or improper dye-gel assembly.

The logics in Figure 7-1 can provide an efficient assembly strategy so that unnecessary trial-and-error can be minimized. The nanoassembled system that Oishi et al. developed displays a multi-stimuli (pH, temperature, and light)-induced release of dye molecules, which is its nanoproperty element. Nanostructural element is its volume-phase transition (changes in the size of the nanoassembled system). They are correlated nicely with each other and with the principles of forced assembly that will be discussed in the next chapter.

7.3.2.3. Hierarchical Assemblies. This subsection shows the assembly of nanoassembled systems through a heterogeneous route with hierarchical mode. This is for case III in Figure 7-1.

Figure 7-5(a) shows the assembly of nanotube/protein nanocomposite for biocompatible materials. Figure 7-2 has a collagen self-assembly building unit. It also shows carbon nanotube having its surface silylated, which made it a fabrication building unit. We thus select two different types of building units for this assembly. And the nature of the two building units is clearly different. Hence, the assembly system here has building units of multiple types and kinds. Figure 7-1 says that a heterogeneous route with a sequential or hierarchical mode can be a better option to choose. The requirement of this nanoassembled system would be properly met when it can take full advantage of collagen.

Collagen has strong directional and asymmetric packing segments that can provide a greater possibility of forming hierarchical structure for the nanocomposite. Hierarchically structured nanocomposite can show greatly improved properties both structure-wise and function-wise. Figure 7-2 also shows that collagen has attractive and repulsive segments as well. By controlling the directional force along with the balance between attractive and repulsive forces, collagens self-assemble in an end-to-end configuration. This is the first step. The next step can be directional, too. The directional force at this time is induced by the rod-shaped collagen aggregate (primary self-assembled aggregate). This makes collagens self-assemble in a side-by-side configuration. The hierarchy of the nanocomposite is generated at this step.

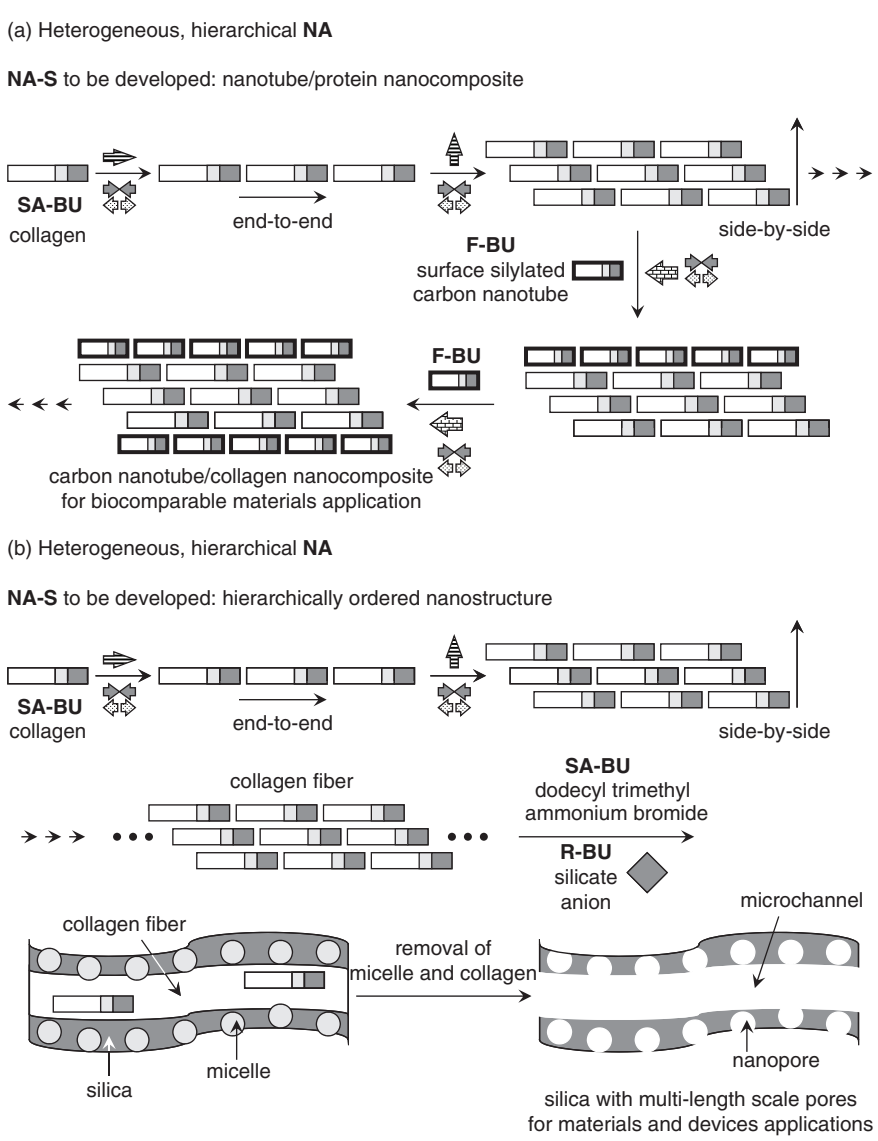


Figure 7-5. Assembly of nanoassembled systems (**NA-S**): case III. **NA** is short for nanoassembly. **SA-BU, F-BU**, and **R-BU** refer to self-assembly, fabrication, and reactive building units, respectively.

So is its morphological chirality. This is through multi-step self-assembly. For collagen, if necessary, this multi-step assembly can continue into higher orders. The other building unit, surface silylated carbon nanotube, can now assemble with the collagen aggregate. This carbon nanotube has its own attractive and repulsive segments that will be balanced with the attractive and repulsive segments of collagen.

The attractive segments from both building units first bring them together, and as the attraction progresses, the repulsive segments also from both building units counterbalance it.

Carbon nanotube does not have a directional segment. However, given its morphology, when it assembles with collagen aggregate, it will generate a conditional directional force, which can help the nanotubes to be aligned on the surface of collagen. This directional force has mainly a capillary force origin. By controlling experimental conditions, the same assembly can be performed on the other side of the collagen aggregate with the nanotube. This is a carbon nanotube/collage nanocomposite. If necessary, assemblies for the higher orders of nanocomposite can be performed. The assembly principle is the same. Considering the hierarchy and chirality of this nanocomposite along with the remarkable mechanical properties of carbon nanotube and the biological properties of collagen, it can show a diverse range of interesting properties. The nanoproperty element should be the primary nanoelement to be characterized. Examination of the nanostructural element also should be performed whenever necessary. Possible options to work with this assembly system would be changing their segmental structures rather than changing their whole structural features. This would mean changing assembly conditions for collagen and changing surface modifying agents for carbon nanotube.

Figure 7-5(b) shows the assembly of hierarchically ordered inorganic nanostructure. Should this type of hierarchical inorganic materials be realized, there would be numerous applications especially in the area of materials and nanoscale devices. Among the building units in Figure 7-2, collagen has the best potential for creating hierarchy. For an additional hierarchy, dodecyltrimethylammonium bromide is used as another building unit. Its primary self-assembled aggregate (micelle) has its size in a much different length scale than that of collagen. This is one of the key points in inducing a morphological hierarchy. The third building unit should be the one that can yield the inorganic nature. Silicate anion is once again an excellent building unit for this. The choice of building units now shows that there are two self-assembly building units (collagen and dodecyltrimethylammonium bromide) and one reactive one (silicate anion). This is the assembly system with multiple types of building units. Given the nature of the building units, a sequential mode is not practical. The hierarchical mode should be the one chosen. Collagen should be the first one to assemble. It will generate larger aggregates so that they can be a substrate for the next step. The assembly of collagen in an end-to-end configuration followed by a side-by-side one is the same as for the previous example. It is a result of the force balance between its own attractive and repulsive segments guided by its own directional segment. This directional assembly can continue until a collagen fiber with desired hierarchy and size is obtained. Chirality is expressed here, too. Typically, the length of a collagen fiber that is induced by the self-assembly *in vitro* can reach the millimeter length scale.

The next step is the assembly of dodecyltrimethylammonium bromide. And it is immediately followed by the addition of silicate anion. (The reverse order of assembly will make it almost impossible to induce an attractive interaction of silicate anion with the surface of dodecyltrimethylammonium bromide micelle.

Silicate anion will be hydrolyzed and condensed on the surface of collagen.) The attractive segments from dodecyltrimethylammonium bromide and collagen attract each other, which means, considering the size difference between the two, on the surface of the collagen fiber. This makes the micelles assemble on the surface of the collagen fiber. Their distribution should be reasonably regular because the attraction is eventually counterbalanced by the repulsive segments from both building units. An assembly of silicate anions followed by this step creates the nanocomposite nanoassembled system through condensation reaction.

Finally, the removal of the organic parts, that is, micelle and collagen fiber, from the nanocomposite will leave the silica part only, and the pores will be generated inside of it. These pores should be hierarchical. One of them is a nanopore that is copied by the micelle, and the other is a micropore with channel morphology that is copied by the collagen fiber.

7.3.3. General Assembly Trends

A general tendency for the assembly with multiple building units (nanoassembly) can be established based on their structural analysis (segmental analysis). This section shows how to make this general tendency and its technical implication. Figure 7-6 is a general description. A proper segmental analysis of nanoassembly building units makes it possible to analyze nanoassembly processes through the scheme of force balance. The horizontal arrow in Figure 7-6 represents the line of force balance between the attractive and repulsive segments of any building units. External forces can be involved as well, depending on the type of assembly system. Both homogeneous all-at-once and heterogeneous sequential assemblies are on this line. Examples (a) and (b) in case I (Figure 7-3) are for the former, and all the examples for case II (Figure 7-4) are for the latter.

Generally speaking, whenever an assembly system takes one of these routes, it is primarily this symmetric force balance that greatly affects the spontaneity of the assembly. The vertical arrow is for an assembly with a strong directional segment. The top end is for a homogeneous successive assembly. Examples (c) and (d) in case I (Figure 7-3) belong to this end. Whenever a directional force is enforced by surfaces, it is more practical to take this route in order to increase the chance of successful assembly. The other end of the arrow represents a heterogeneous hierarchical assembly, which is for case III (Figure 7-5). Whenever there are directional and asymmetric packing segments involved for a certain assembly, this route can provide a better chance of a satisfactory assembly outcome. Along with this discussion, it will be useful to refer to an article by Klavins (2003) that derives the equations of motion for the control of the self-assembly of colloidal particles, specifically for how to avoid structural flaws in the assembled systems and how to assemble terminating and asymmetric structures.

7.3.3.1. Homogeneous Assemblies. A general trend for the assembly in example (b) of case I (Figure 7-3) is shown in Figure 7-7. It is to control surface plasmon resonance by tuning the homogeneous assembly. Starting from the gold

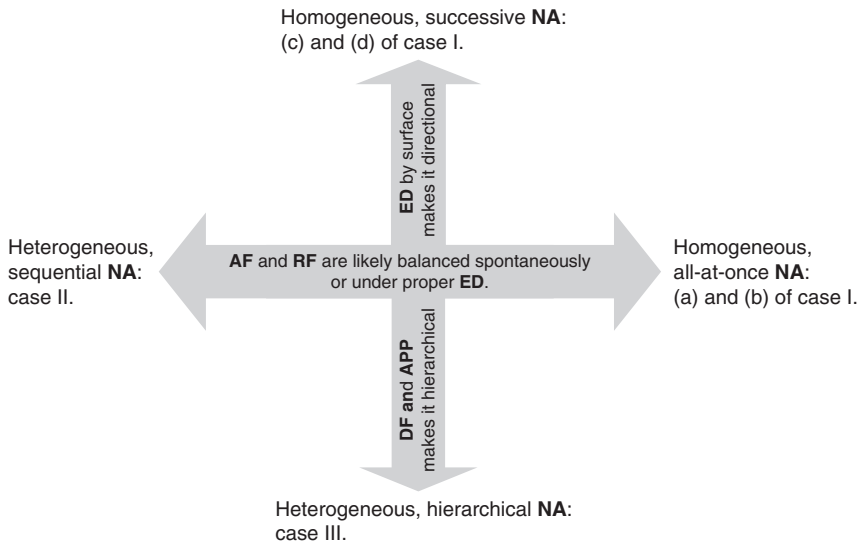


Figure 7-6. General trend for the assembly with multiple building units. **NA** is short for nanoassembly. **AF, RF**, and **DF** refer to attractive, repulsive, and directional forces, respectively. **APP** is asymmetric packing process. **ED** is external force–induced directional factor.

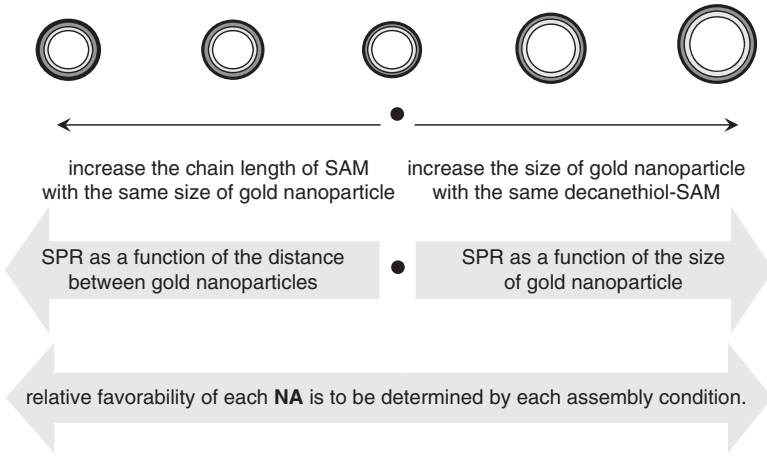

increase the chain length of SAM
with the same size of gold nanoparticle
increase the size of gold nanoparticle
with the same decanethiol-SAM
SPR as a function of the distance
between gold nanoparticles
SPR as a function of the size
of gold nanoparticle
relative favorability of each **NA** is to be determined by each assembly condition.

Figure 7-7. Control of surface plasmon resonance (SPR) by tuning homogeneous nanoassembly (**NA**): for case I (Figure 7-3(b)). SAM is self-assembled monolayer.

nanoparticle at the center, one way to control surface plasmon resonance is to increase the size of the gold nanoparticle while keeping the same decanethiol self-assembled monolayer on its surface. Then, surface plasmon resonance will be a function of the size of the gold nanoparticle. Another way is to increase the chain length of alkanethiols that are assembled on the surface of the gold

nanoparticle while keeping the size of the gold nanoparticle the same. Surface plasmon resonance will be controlled as a function of the distance between the gold nanoparticles. Relative favorability of each assembly system is determined by each assembly condition. Figures 3-6 and 3-7, which explained the general tendency of colloidal self-assembly, can provide some specific ideas to tune the force balance between the attractive and repulsive segments of the gold nanoparticles.

7.3.3.2. Heterogeneous Assemblies I. Figure 7-8 shows a general trend for example (a) of case II (Figure 7-4). The lattice structure of binary colloidal crystal can be controlled by tuning a heterogeneous assembly. There are two building units for the assembly of binary colloidal crystal: polystyrene colloidal self-assembly building unit and decanethiol-protected gold nanoparticle fabrication building unit. This indicates that there can be two options for the control of the lattice structures of the binary colloidal crystal. The first one is to change the size ratio of polystyrene particle to gold nanoparticle. This is shown in the upper part of the figure. The arrow is the direction of decreasing size ratio. This change mainly affects the overall lattice morphology, and there can be a critical point where the assembly of the binary colloidal crystal is no longer possible. When the size of polystyrene particle becomes comparable to that of gold nanoparticle, it can no longer provide enough space wherein the gold nanoparticles can be arranged. Considering the same

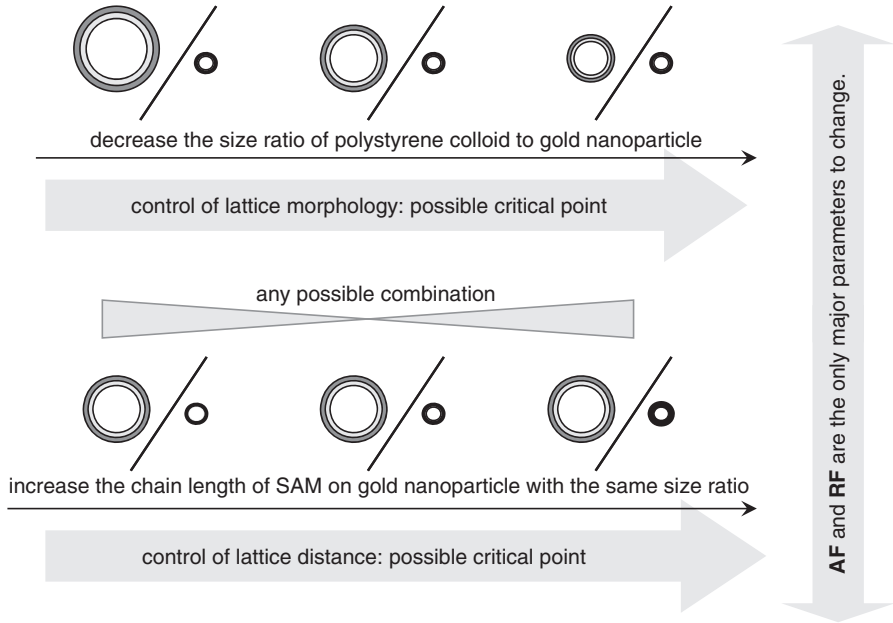

decrease the size ratio of polystyrene colloid to gold nanoparticle
control of lattice morphology: possible critical point
any possible combination
increase the chain length of SAM on gold nanoparticle with the same size ratio
control of lattice distance: possible critical point
AF and RF are the only major parameters to change.

Figure 7-8. Control of the lattice structure of binary colloidal crystal by tuning heterogeneous nanoassembly: for case II (Figure 7-4(a)). **AF** and **RF** refer to attractive and repulsive forces, respectively. SAM is self-assembled monolayer.

relative strength of their attractive and repulsive forces, it may not be practical to obtain a well-arranged binary colloidal crystal.

The second option is to control the chain length of the alkanethiols that are assembled on the surface of the gold nanoparticle while keeping the same size ratio. The bottom part of the figure shows this. The arrow is the direction increasing the chain length. This can allow us to control the lattice distance. It may have a critical point, too, as the chain length is increased. The increased chain length eventually will reach the point where it cannot sustain the attractive force between polystyrene and gold particles any longer. The polystyrene particle would begin to immerse into the brushes of hydrocarbon chains. Any possible combination of these two options can be another option to choose. Whatever combination is chosen, the force balance between the attractive and repulsive segments from the two building units is the major parameter to change.

7.3.3.3. Surface Assemblies. Figure 7-9 shows a homogeneous assembly at solid surfaces that is for example (d) of case I (Figure 7-3). There is only one building unit, which is gold vapor reactive building unit. Silicon is a substrate. However, since this silicon is the one that provides a directional force, which is the critical factor in achieving the main object, and since there is not much room to play in terms of changing the attractive segment of gold vapor, it is important for this particular system to pay attention to the substrate when draws a general trend.

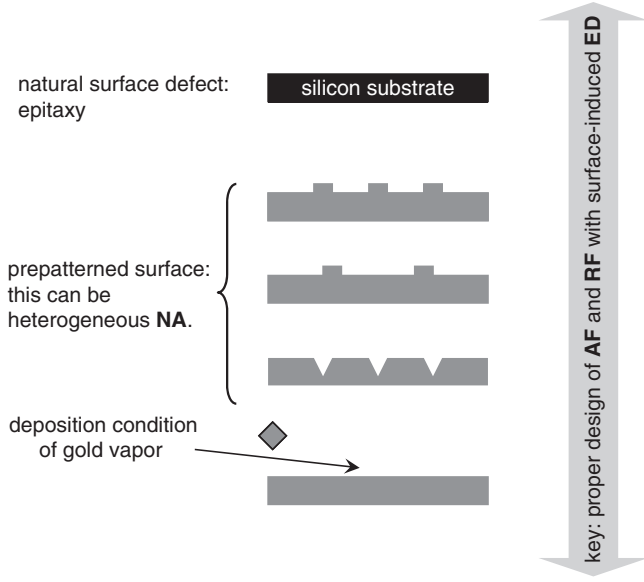


Figure 7-9. Control of surface pattern by tuning homogeneous nanoassembly (**NA**): for case I (Figure 7-3(d)). **AF** and **RF** refer to attractive and repulsive forces, respectively. **ED** is external force–induced directional factor.

First, an assembly can take advantage of naturally occurring surface defects on the silicon surface so that gold can have a pattern by following the pattern of the defects. This is called *epitaxial deposition*. Also, silicon surface can be prepatterned to provide regularly patterned surface structures that can have a high affinity with gold vapor. Regularly carved grooves can provide a confinement for gold vapor. This second option can be a heterogeneous assembly. A different distance between the surface patterns, different surface roughness, and various structures of the pattern will be important structural parameters to control. For gold vapor, there may be only one option, which is varying the deposition condition. This includes deposition time and temperature, beam velocity and flux, and deposition angle. Whatever option is chosen, the key to the desired gold nanopattern is proper design of the force balance between the attractive segments from gold and silicon and the repulsive segment from silicon. A directional force induced by silicon is responsible for the directionality of the nanoassembled system.

7.3.3.4. Heterogeneous Assemblies II. Figure 7-10 shows a heterogeneous hierarchical assembly for example (b) of case III (Figure 7-5). It is to control the dual porosity of porous silica. There are three building units. Silicate anion is fixed since the nanoassembled system is silica. The other two are collagen and dodecyltrimethylammonium bromide. The first option is to change the degree of the self-assembly of collagen, which is possible by tuning its segmental structure. This allows us to control the details of the silica microchannel and its overall

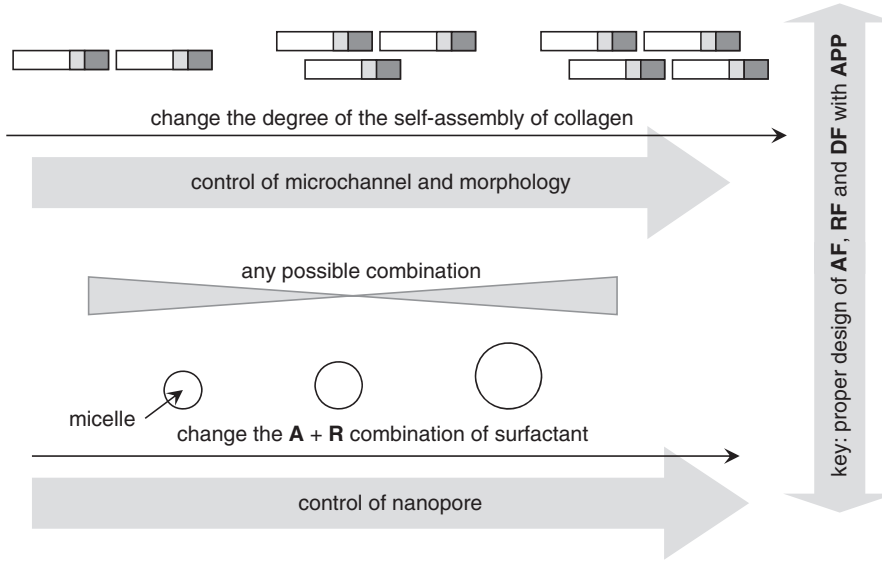

change the degree of the self-assembly of collagen
control of microchannel and morphology
any possible combination
micelle
change the A + R combination of surfactant
control of nanopore
key: proper design of AF, RF and DF with APP

Figure 7-10. Control of the dual porosity of porous silica by tuning heterogeneous nanoassembly: for case III (Figure 7-5(b)). **A** and **R** refer to attractive and repulsive segments, respectively. **AF, RF**, and **DF** refer to attractive, repulsive, and directional forces, respectively. **APP** is asymmetric packing process.

morphology. The second option is to change the segmental structure of dodecyltrimethylammonium bromide, which means to have different length of hydrocarbon chain while keeping the same trimethylammonium head group. This does not change the force balance with collagen significantly. But it will change the size of the cationic micelles that assemble on the surface of the collagen aggregates, which in turn will change the size of the nanopore accordingly. For an actual assembly, any possible combination between these two options can be exercised. The key is proper structural design that can satisfy the force balance between the attractive and repulsive segments from both building units and with the directional and asymmetric packing segments from collagen.

7.4. COLLECTION OF NANOASSEMBLED SYSTEMS I

Table 7-1 lists the collection of the nanoassembled systems that frequently appear in the literature. Some of these are assembled with a single nanoassembly building unit (for example, colloidal crystal of single component). But most of them are assembled with multiple building units. The table also presents the main assembly principles for each system. Some of these can be assembled both in solution and at surface. But for many, the assembly should be exclusively either in solution or at surface in order to ensure proper assembly. Assembly routes are indicated for each system. This is not an absolute condition for each system. For example, almost all of the deposited films can be assembled more effectively by choosing homogeneous assembly. However, there often can be a specific assembly situation or system requirement that can be better solved by heterogeneous assembly. For a specific case, when the film is deposited on a solid surface with metal ions and ligand molecules, the surface complexation that is one of the keys to achieve

TABLE 7-1. Collection of nanoassembled systems and their main assembly principles. Surface and solution indicate assemblies on surface and in solution, respectively; ho and he refer to homogeneous and heterogeneous assemblies, respectively.

Nanoassembled System	Assembly Principle
colloidal crystal	surface/solution: ho, he
inverse colloidal crystal	surface/solution: he
chemical vapor deposited film	surface: ho
physical vapor deposited film	surface: ho
photochemical vapor deposited film	surface: ho
metal-organic chemical vapor deposited film	surface: ho
plasma-enhanced chemical vapor deposited film	surface: ho
ion-plating vapor deposited film	surface: ho
laser ablation vapor deposited film	surface: ho
nanocomposite	surface/solution: he
organic-inorganic hybrid material	solution: he
nanoporous material	solution: he
mesoporous material	solution: he
molecular sieve (zeolite)	solution: he
metal-organic framework	solution: he

ordered metal-ligand films can be better controlled via heterogeneous assembly. If this becomes the case, sequential or hierarchical assembly could be a better option than successive or all-at-once assembly. Despite this occasional exception, by referencing this table with the segmental structures of each self-assembly (Section 1.5) and nanoassembly building units (Section 2.7), the nanoassembly processes in the literature that sometimes look random and often lack the effects of different assembly routes could be understood from a more mechanistic basis. This in turn would help in designing a more effective assembly system and route for a given nanoassembled system.

7.5. COLLECTION OF NANOPOROUS SOLIDS

Among the nanoassembled systems that are assembled with multiple building units, nanoporous solids may have the most diverse ranges of origins and thus diverse ranges of properties and corresponding applications. Table 7-2 collects various nanoporous solids and their main building units and assembly principles. Given the diversity of each porous solid, detailed building units (primary building units) cannot be specified. Instead, the table gives the main building units that compose each of the porous solids. Some general idea about the similarity and difference between the porous solids could be obtained from this. Assembly principles for each porous solid are also somewhat different from those discussed in this chapter. These are the specific chemical principles that govern various steps of the assembly for each porous solid. It thus can help reveal how the common chemical processes work between the building units during nanoassembly. Some studies in the literature do not clarify this important aspect. More discussion will be found in Chapter 11.

TABLE 7-2. Collection of nanoporous solids, and their main building units and assembly principles.

Porous Solid	Building Unit	Assembly Principle	Nature	Common Name
zeolite, natural	many natural minerals	nucleation, crystallization, mineralization	crystalline	
zeolite, synthetic	synthetic minerals	nucleation, crystallization, molecular templating	crystalline	Table 7-3
biomineral	natural biominerals	biomineralization	crystalline	
mesoporous material	silica, aluminosilica, titania, ceria, hafnia	nucleation, condensation, soft templating	amorphous	MCM series, SBA series
mesoporous carbon	carbon	condensation, pyrolysis, hard templating	amorphous	
metal-organic framework	metal ion, dicarboxylic acid	controlled ionic assembly	crystalline	Table 7-4

TABLE 7-3. Collection of synthetic zeolites.

Class Name
zeolite A
zeolite H
zeolite L
zeolite X
zeolite Y
zeolite β
borosilicate zeolite
high-silica zeolite
silicalite zeolite
aluminophosphate (AlPO) zeolite
silicoaluminophosphate (SAPO) zeolite
titanosilicate zeolite
vanadosilicate zeolite
cancranite-type zeolite
chabasite-type zeolite
clinoptilolite-type zeolite
erionite-type zeolite
faujasite-type zeolite
ferrierite-type zeolite
mordenite-type zeolite
pentasil-type zeolite
ZSM-type zeolite

Nanoporous solids can have either a crystalline or amorphous nature. Those with a crystalline nature are more stable and their overall structures are better defined. But they sometimes lack the flexibility and functionalization capability. Those with an amorphous nature are the opposite. They are less stable (especially hydrothermal stability) and their overall structures are less defined. But they have better flexibility in terms of the diversity of the structures, and their surfaces are easier to functionalize with common ligands. *MCM* and *SBA series* are the well-known names of mesoporous solids. These names appear in the broad range of the literature. They are mainly silica or aluminosilica (also many other metal oxides), whose mesopores (the same as nanopores) are copied (templated) by the self-assembled aggregates (micelles) of surfactants or polymers. More details on these will also be found in Chapter 11. There is more on synthetic zeolites and metal-organic frameworks in Tables 7-3 and 7-4, respectively.

7.5.1. Synthetic Zeolites

A full description of synthetic zeolites is beyond the scope of this book. Natural zeolites are also so diverse that they will not be discussed here. Table 7-3 lists the collection of synthetic zeolites that appear most often in the literature. This is certainly not a full list, but it covers most of the representative groups. Most of the synthetic zeolites are aluminosilica or pure silica. Many others are named after their main building units. All of the synthetic zeolites are assembled via molecular templating. More precisely, they are assembled through heterogeneous sequential

TABLE 7-4. Collection of metal-organic frameworks, and their common names and main assembly building units.[1] IRMOF, MOF, MIL, and ZIF are short for isoreticular metal-organic framework, metal-organic framework, material of Institute Lavoisier, and zeolitic imidazolate framework, respectively.

Name	Building Unit
IRMOF-1 (MOF-5)	zinc ion+1,4-benzenedicarboxylic acid
IRMOF-2	zinc ion+2-bromo-1,4-benzenedicarboxylic acid
IRMOF-3	zinc ion+2-amino-1,4-benzenedicarboxylic acid
IRMOF-6	zinc ion+bicyclo[4.2.0]octa-1,3,5-triene-2,5-dicarboxylic acid
IRMOF-7	zinc ion+1,4-naphthalenedicarboxylic acid
IRMOF-8	zinc ion+2,6-naphthalenedicarboxylic acid
IRMOF-9 (IRMOF-10)	zinc ion+[1,1′-biphenyl]-4,4′-dicarboxylic acid
IRMOF-11 (IRMOF-12)	zinc ion+4,5,9,10-tetrahydro-2,7-pyrenedicarboxylic acid
IRMOF-13 (IRMOF-14)	zinc ion+2,7-pyrenedicarboxylic acid
IRMOF-15 (IRMOF-16)	zinc ion+[1,1′:4′,1″-terphenyl]-4,4″-dicarboxylic acid
IRMOF-18	zinc ion+2,3,5,6-tetramethyl-1,4-benzenedicarboxylic acid
IRMOF-20	zinc ion+thieno[3,2-b]thiophene-2,5-dicarboxylic acid
IRMOF-993	zinc ion+9,10-anthracenedicarboxylic acid
MOF-1	zinc ion+1,4-benzenedicarboxylic acid+1,4-diazabicyclo[2.2.2] octane
MOF-14	copper ion+5'-(4-carboxyphenyl)[1,1′:3′,1″-terphenyl]-4,4″-dicarboxylic acid
MOF-74	zinc ion+*N,N*-dimethylformamide+2,5-dihydroxy-1,4-benzenedicarboxylic acid
MOF-177	zinc ion+4,4′,4″-benzene-1,3,5-triyl-tribenzoic acid
MOF-180	zinc ion+4,4′,4″-(benzene-1,3,5-triyl-tris(ethyne-2,1-diyl))tribenzoic acid
MOF-200	zinc ion+4,4′,4″-(benzene-1,3,5-triyl-tris(benzene-4,1-diyl)) tribenzoic acid
MOF-205	zinc ion+4,4′,4″-benzene-1,3,5-triyl-tribenzoic acid+2,6-naphthalenedicarboxylic acid
MOF-210	zinc ion+4,4′,4″-(benzene-1,3,5-triyl-tris(ethyne-2,1-diyl))tribenzoic acid+biphenyl-4,4′-dicarboxylic acid
MIL-47	vanadium ion+1,4-benzenedicarboxylic acid
MIL-53	chromium ion+1,4-benzenedicarboxylic acid
MIL-89	iron ion+(2E,4E)-2,4-hexadienedioic acid+methanol
MIL-100	chromium ion+1,3,5-benzenetricarboxylic acid
MIL-101	chromium ion+1,4-benzenedicarboxylic acid
IRMOF(Mg)-1	magnesium ion+1,4-benzenedicarboxylic acid
IRMOF(Be)-1	beryllium ion+1,4-benzenedicarboxylic acid
HKUST-1	copper ion+1,3,5-benzenetricarboxylic acid
ZIF-8	zinc ion+2-methlyl-1H-imidazole
ZIF-11	zinc ion+1H-benzimidazole
ZIF-68	zinc ion+1H-benzimidazole+2-nitro-1H-imidazole
ZIF-69	zinc ion+5-chloro-1H-benzimidazole+2-nitro-1H-imidazole
ZIF-71	zinc ion+4,5-dichloro-1H-imidazole

[1]For more about the properties and applications of these materials, please see Horike et al., 2009.

assembly of at least two different building units (inorganic precursor and small organic molecules, mostly short-chain quaternary ammonium). The most critical difference from the above nanoporous solids is that the small molecules do not self-assemble during this assembly. It is the small molecule itself that copies its molecular sizes into the zeolite solids.

7.5.2. Metal-Organic Frameworks

Metal-organic frameworks are the youngest members of the nanoporous solid family. They are also a new class of nanoporous solid. No templating process is involved during their assembly, neither by small molecules nor by micelles. The delicately balanced geometrical nature of the nanoassembled system (metal-organic framework) provides well-defined and well-arranged nanopores. As for the zeolites, a full description of metal-organic frameworks is beyond the scope of this book. However, Table 7-4 collects most of the metal-organic frameworks that had been published by the end of 2010. But considering their ease of assembly and flexibility and the diversity of their potential building units, it is certain that many more will be forthcoming. The main building units for each metal-organic framework are also shown in the table. Some studies skip the information related to the building units; thus this table helps us understand the assembly process of each of the metal-organic frameworks and their interaction with other molecules. More details on the assembly of metal-organic frameworks will be discussed in Figure 13.2(f).

7.6. SUMMARY

This chapter discussed how to come up with an effective assembly strategy for a given nanoassembly. It showed that:

1. Many nanoassembled systems are assembled with multiple types and kinds of building units.
2. A careful selection and structural analysis of their building units (segmental analysis) can help in designing a proper assembly route.
3. It is not absolute, but by following it, the assembly can be more effective.
4. The assembly principles in Chapters 3 through 6 are directly applied in each step of the assembly.
5. A general tendency, though somewhat crude, could help in designing future nanoassembled systems in a systematic manner.

Most of the assemblies in this chapter take place spontaneously. But there are many other nanoassembled systems that cannot be assembled through a spontaneous process. This is when external forces can play an important role. This is the key issue of the next chapter.

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8

Directed and Forced Assemblies

8.1. ASSEMBLY ISSUE

As discussed in the previous chapter, the first step in the design of nanoassembly system is identifying its building units. This should be followed by careful analysis of their structures (*segmental analysis*: see Subsection 1.2.2 for the details). This approach can tell us whether and how certain nanoassembly building units would assemble. Ideally, it would be best, in terms of effectiveness and efficiency, if the building units are assembled under a given condition without any need of additional reagents that will have to be removed from the nanoassembled system afterward or without any need of external forces to modify the force balance. This, in other words, means that spontaneous assembly is always the best route to take for any assembly system. However, for many assembly systems, their building units do not always show ideal segmental structures for spontaneous assembly. Also, in many cases, even though the building units can assemble spontaneously, it is possible that the properties of the nanoassembled system could be improved by varying assembly conditions. Moreover, it can be necessary that the nanoassembled system is modified to express the desired nanoproperties. This is when external forces come into play. External forces are proven to have a range and strength comparable with the interactions between most of the building units. And we have well-studied means to control most of them. Applying a proper external force to building units that have little structural favorability for spontaneous assembly can make the assembly very practical. This is called a *forced assembly*. When the

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directional assembly is more emphasized or when the external forces are applied to enhance the directionality of spontaneous assembly, it is called *directed assembly*. That being said, the main question to ask in this chapter is:

How can the necessity of external forces be determined for a given set of nanoassembly building units?

This yields follow-up issues:

How can the most effective external force be determined?

Can external forces achieve specific purposes not otherwise possible?

If so,

What are the specific criteria to apply them?

A directed or forced assembly can nicely expand the availability of building units. They expand not only the scope of the building units beyond the restriction of their segmental structures, but the practicality of the building units as well. This is directly related to the improvement in effectiveness and efficiency of assembly. As will be shown in the third part of the book, many of the nanoproperties, nanostructures, and nanodevices/nanomachines can take great advantage by expanding assembly means via directed or forced assembly. The article by Grzelczak et al. (2010) provides an overview of directed self-assembly of nanoparticles. As stated in Section 7.1, *assembly* in this chapter means *nanoassembly* (for details, see Section 2.1). By the definition shown in Section 2.6, the assembled systems of nanoassembly building units are nanoassembled systems. Nanoassembled systems include self-assembled aggregates and are a part of nanotechnology systems.

8.2. GENERAL OVERVIEW

A general overview of this chapter is shown in two separate figures. Figure 8-1 shows how to determine a spontaneous or forced (or directed) assembly route. Figure 8-2 shows how to identify a proper external force for a specific nanoassembly system.

The first step to determine whether to choose a spontaneous or a forced assembly is selecting the building units. As with Figure 7-1, the nature of either the nanoassembled system or the building units that can properly assemble it has to be decided. This can be reversed. For some cases, the nature of the nanoassembled system to be developed is clear, but not many building units are available. In other cases, there can be building units that look sound but are not practical enough to be assembled into the desired nanoassembled system. Once proper building units are identified, the determination of proper assembly mode should follow. Figure 7-1 showed the precise steps for this. If all-at-once assembly is chosen, the next question to ask is whether the building units can satisfy the force balance between

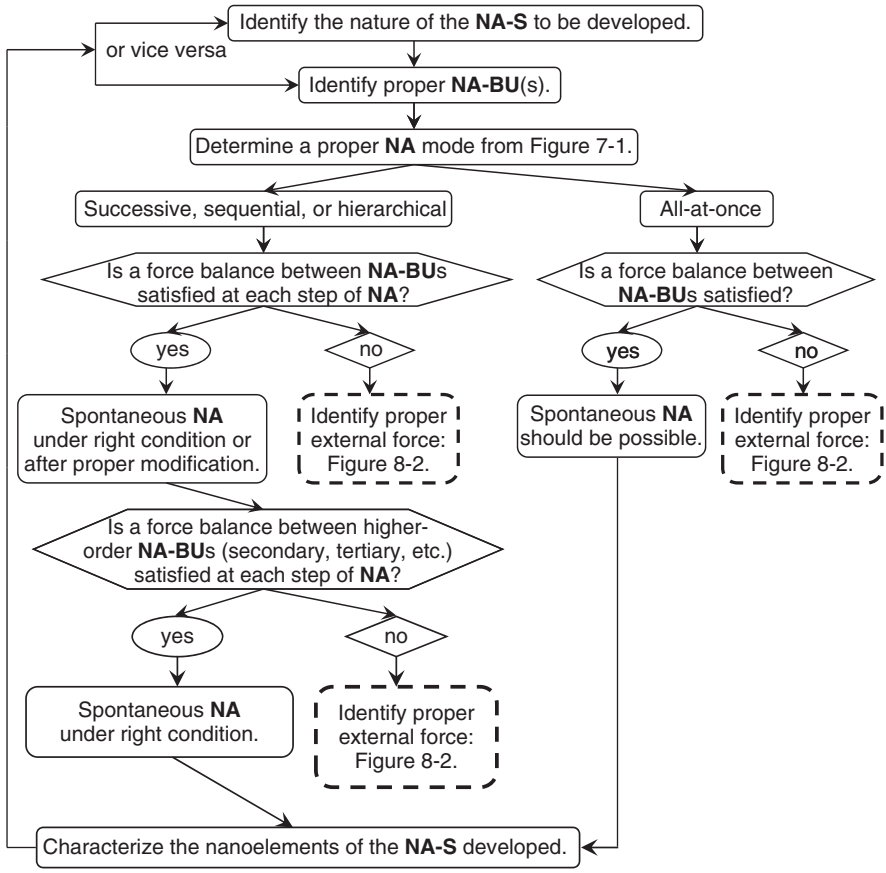

Identify the nature of the NA-S to be developed.
or vice versa
Identify proper NA-BU(s).
Determine a proper NA mode from Figure 7-1.
Successive, sequential, or hierarchical
All-at-once
Is a force balance between NA-BUs satisfied at each step of NA?
Is a force balance between NA-BUs satisfied?
yes
no
yes
no
Spontaneous NA under right condition or after proper modification.
Identify proper external force: Figure 8-2.
Spontaneous NA should be possible.
Identify proper external force: Figure 8-2.
Is a force balance between higher-order NA-BUs (secondary, tertiary, etc.) satisfied at each step of NA?
yes
no
Spontaneous NA under right condition.
Identify proper external force: Figure 8-2.
Characterize the nanoelements of the NA-S developed.

Figure 8-1. General overview of the design of directed and forced assemblies. **NA, NA-BU**, and **NA-S** are short for nanoassembly, nanoassembly building unit, and nanoassembled system, respectively.

them. Their segmental structures can answer this question. If the answer is no, the best option to use is a proper external force. Figure 8-2 shows the steps to take for this. If, however, the answer is yes, there will be no need of external force. A spontaneous assembly should be possible. If successive, sequential, or hierarchical assembly is identified as the proper choice, the next question to ask is whether the force balance can be achieved at each step of assembly process. If the answer is no, the steps in Figure 8-2 should be taken to identify a proper external force. If the answer is yes, a spontaneous assembly should be possible. The right experimental condition should be identified or, if possible, minor modifications to meet the force balance could be performed. The next question is whether there is a proper force balance between higher-order building units. (*Higher-order nanoassembly* is the same concept as *higher-order self-assembly* in Chapter 4.) If the answer is no, the

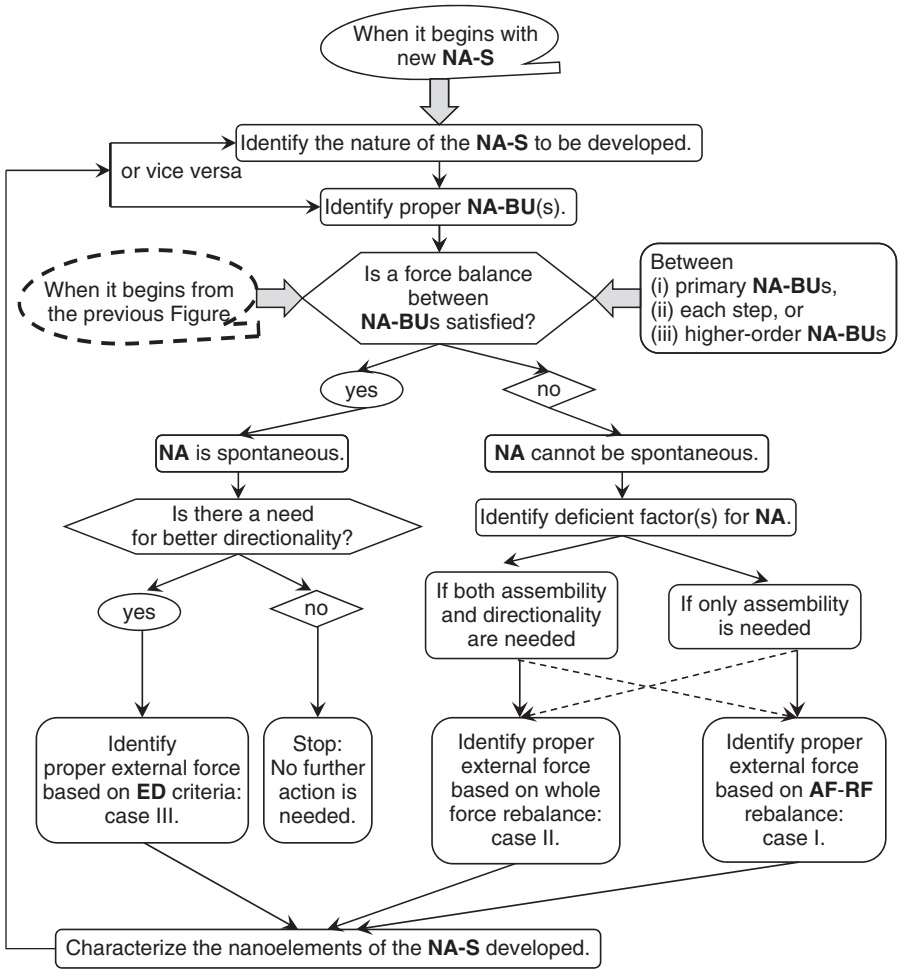

When it begins with new NA-S
Identify the nature of the NA-S to be developed.
or vice versa
Identify proper NA-BU(s).
When it begins from the previous Figure
Is a force balance between NA-BUs satisfied?
Between (i) primary NA-BUs, (ii) each step, or (iii) higher-order NA-BUs
yes
no
NA is spontaneous.
NA cannot be spontaneous.
Is there a need for better directionality?
Identify deficient factor(s) for NA.
yes
no
If both assembility and directionality are needed
If only assembility is needed
Identify proper external force based on ED criteria: case III.
Stop: No further action is needed.
Identify proper external force based on whole force rebalance: case II.
Identify proper external force based on AF-RF rebalance: case I.
Characterize the nanoelements of the NA-S developed.

Figure 8-2. General overview of the selection of proper external forces for directed and forced assemblies. **NA, NA-BU**, and **NA-S** are short for nanoassembly, nanoassembly building unit, and nanoassembled system, respectively. **AF** and **RF** refer to attractive and repulsive forces, respectively. **ED** is external force–induced directional factor.

process should continue on to Figure 8-2. If, however, the answer is yes, a spontaneous assembly without any external forces should be possible. The last step is to characterize the nanoelements (for details, see Section 2.3). If the desired nanoelements are not achieved, the assembly process should go back to the beginning to look for possible options to adjust the building units.

Figure 8-2 shows the procedure for the selection of a proper external force where the analysis of a certain assembly system reveals that its assembly can be achieved only (or better) through a forced (or directed) assembly. In addition, this diagram

can be useful when an assembly still can take place spontaneously but there is a possibility that the nanoassembled system can be improved when assembled under a certain external force.

First, the nature of the nanoassembled system has to be identified, which should be followed by the selection of its building units. As for the diagram in Figure 8-1, this can be reversed. The next question is whether there is a satisfactory force balance between the building units. The force balance here includes the one between the primary building units, the one between each step of assembly, and the one between the higher-order building units. If this step begins from the previous figure (three bold dot-lined boxes), the same question is asked by following any of the boxes. If the answer is no, the assembly cannot be spontaneous.

The deficient assembly factors should be determined next. The importance of the segmental analysis of building units can be stressed once more here. If this analysis finds that only assembility is needed for the assembly system, a proper external force can be identified based on the rebalance between attractive and repulsive forces. (The word *assembility* is used to refer to "the degree of assembly capability." *Assemblability* might be a decent choice. But that seems more likely to imply the mechanical assembly of different parts on an industrial scale.) This means that there may already be a force balance between attractive and repulsive segments, but somehow it does not give enough assembly power to the assembly system. Thus a proper external force should intervene to help achieve a satisfactory force balance between the building units. This will be designated as *case I* for the discussion in the next few sections. If the analysis shows that not only is assembility needed but a directionality of the assembly process is required as well, the choice of external force becomes complicated. It should be based on the whole force rebalance. In many cases, this means that the external force should reinforce the existing force balance and often help overcome it to induce a new balance. This is *case II*. For some assembly systems, cases I and II can be interchangeable. There can be an assembly system whose deficient factor is only assembility, but which can be achieved through a whole force rebalance. And there can be an assembly system where both assembility and directionality are needed, but which is achievable through the attractive–repulsive force rebalance. If the answer to the question about the force balance between the building units is yes, the assembly is spontaneous. There is no need of any external force. If, however, the purpose of the nanoassembled system can be better met with an enhanced directionality, the process should continue to identify a proper external force. For this specific situation, the choice of external force should be based only on an external force–induced directional factor (for details, see Subsection 1.2.2.2). There is no need to disturb the existing force balance. This is *case III*. If there is no need to enhance the directionality, the process stops here. As with the previous figure, whatever external force is selected, once a nanoassembled system is obtained, its nanoelement has to be characterized to see whether its intended purpose is met. If it turns out that this is not the case, the whole process should go back to the beginning. The details about the types and natures of various external forces can be found in Lee (2008).

8.3. ASSEMBLY PRINCIPLES

8.3.1. Analysis of Building Units

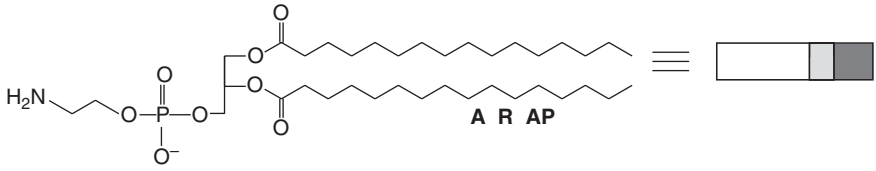
Figure 8-3 shows nanoassembly building units. The symbols for each building unit are the same as those in Figure 7-2.

Figure 8-3(a) shows molecular self-assembly building units, and Figure 8-3(b) has colloidal self-assembly building units. 1,2-dipalmitoyl-*L*-α-phosphatidyl ethanolamine is another typical phospholipid. Its segmental structure is almost identical to 1,2-dipalmitoyl-*L*-α-phosphatidyl choline (Figure 5-4). It has attractive, repulsive, and asymmetric packing segments. Bis(2-ethylhexyl) sodium sulfosuccinate, commonly known as Aerosol-OT, is a bulky anionic surfactant whose characteristic molecular structure is ideal to induce reverse micelles in aqueous solutions. The bulky hydrocarbon chain part should be assigned as its attractive segment since it can generate an attractive hydrophobic force. The anionic head group acts like a typical ionic group. The bulky attractive segment affects only the degree of the electrostatic repulsive force but not its nature. Hence, this head group should be assigned as its repulsive segment. Bis(2-ethylhexyl) sodium sulfosuccinate has three chiral carbons, which should be assigned as asymmetric packing segments, if it is a pure enantiomer. However, none of the known Aerosol-OT molecules used in the literature are pure enantiomers. All of them are available in the forms of a mixture. Thus, even though there may be some degree of local asymmetric packing during the assembly caused by these chiral carbons, none of the known assembled systems of Aerosol-OT shows any structural characteristics induced by these chiral carbons. It can be understood, in terms of the segmental analysis, that the degree and direction of the asymmetric packing are random over the assembled system and thus counterbalance each other. This is the main reason that the asymmetric packing segments are not assigned for this building unit.

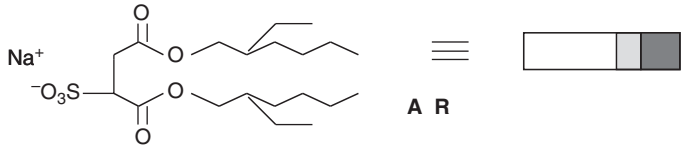
The third molecular building unit is cetyltrimethylammonium chloride. Being almost identical to dodecyltrimethylammonium bromide in Figure 7-2(a), its long hydrocarbon chain is an attractive segment and the trimethylammonium group is a repulsive segment. Three colloidal building units are next. Poly(methyl methacrylate) (PMMA) colloidal particle is assumed to have a surface charge, which makes it have both attractive and repulsive segments. The polystyrene colloidal particle in Figure 7-2(a) was assumed to retain its natural surface charges so that it had both attractive and repulsive segments. However, polystyrene colloidal particle here is assumed to have just a minimal amount of surface charges. It thus should have an attractive segment that is van der Waals force, but the repulsive segment becomes negligible. Colloidal building units with this type of segmental structure often carry an important technical advantage. For the third colloidal building unit, one of the Keggin polyoxometalate clusters is chosen. Their novel properties promise diverse applications in nanotechnology. Tungstomanganatesilicate with its composition of $MnSiW_{11}O_{40}^{8-}$ will represent this group in this chapter. Its colloidal size suggests that it should have van der Waals force, which should then be assigned as its

(a) **SA-BU**: molecular:

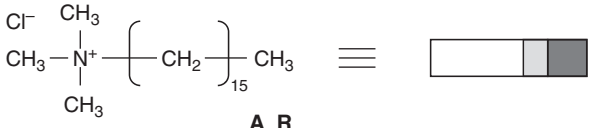
1,2-dipalmitoyl-*L*-α-phosphatidylethanolamine (DPPE)



Aerosol OT: bis(2-ethylhexyl) sodium sulfosuccinate



cetyltrimethyl ammonium chloride (CTAC)



(b) **SA-BU**: colloidal

poly(methyl methacrylate) (PMMA) colloidal particle with surface charge

polystyrene (PS) colloidal particle with minimal surface charge

Keggin polyoxometalate cluster: tungstomanganatesilicate ($MnSiW_{11}O_{40}^{8-}$)

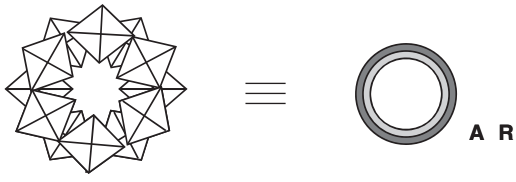
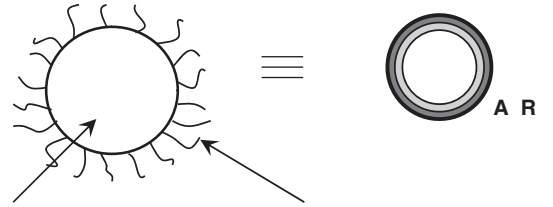


Figure 8-3. Building units. **SA-BU, F-BU**, and **R-BU** refer to self-assembly, fabrication, and reactive building units, respectively. **A, R**, and **AP** refer to attractive, repulsive, and asymmetric packing segments, respectively.

(c) **F-BU**

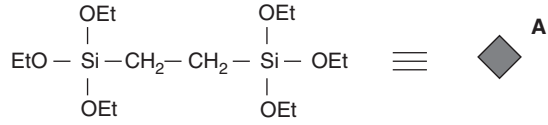
dodecanethiol-protected silver nanoparticle

poly(methyl methacrylate) colloidal particle, surface alkylated {with poly(12-hydroxystearic acid)}



(d) **R-BU**

1,2-bis(triethoxysilyl) ethane



titanium tetrachloride

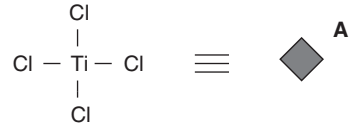


Figure 8-3. (*Continued*)

attractive segment. The nature of its composition provides enough surface charges to give this particle a repulsive segment.

Figure 8-3(c) has two fabrication building units. Dodecanethiol-protected silver nanoparticle is a silver nanoparticle whose surface is modified with 1-dodecanethiol self-assembled monolayers. Its segmental structure is the same as decanethiol-protected gold nanoparticle in Figure 7-2(b). The only difference is that it is now

a silver nanoparticle and has slightly longer hydrocarbon chains on its surface. It thus has both attractive and repulsive segments. The next one is poly(methyl methacrylate) colloidal particle. Unlike the case of the same colloidal particle for the self-assembly building unit in Figure 8-3(b), the surface of this particle is modified with hydrocarbon chains. A simple surface treatment such as surface alkylation or dispersion polymerization can be used for this. This type of colloidal particle is useful for many nanoassembly processes. Its segmental structure should be the same as dodecanethiol-protected silver nanoparticle. van der Waals force is its attractive segment and a steric repulsive force caused by the hydrocarbon chains becomes its repulsive segment.

Figure 8-3(d) has two reactive building units. 1,2-bis(triethoxysilyl) ethane is selected since it can represent the assemblies of silyl group–based building units. These produce many diverse nanostructures and nanoporous organic-inorganic hybrid materials. Its segmental structure can provide good insight into the assemblies of other reactive group–based building units, too. The ethane group in the middle is not assigned as any segment. Unless it is long enough, its role as an attractive segment would be minimal compared with other attractive segments. However, if it is long enough or has strong attractive force generators such as benzene or diphenyl group, which is actually the case for many building units, it should be assigned as an attractive segment. With the same logic as for the silicate anion in Figure 7-2(c), the two triethoxysilyl groups become its attractive segment. A condensation reaction between silanol groups during assembly brings this building unit together. Titanium tetrachloride is used as a source for titanium metal. The same logic is applied here as well. It has only an attractive segment.

8.3.2. Assembly under External Forces

Representative examples for each of the three cases in Figure 8-2 are presented in this section. The building units are limited to those in Figure 8-3 with occasional modifications. A particular purpose of the nanoassembled system is indicated for all examples. However, it is not uncommon that the nanoassembled system that is developed with a specific purpose actually finds an unexpected application.

8.3.2.1. Forced Assemblies. Figure 8-4 shows three examples for systems that need forced assembility for their reasonable assembly. They thus belong to case I of Figure 8-2.

Figure 8-4(a) is the first example. Its purpose is to have a photonic band gap device. We use poly(methyl methacrylate) colloidal particle as a building unit. Polystyrene colloidal particle and the two fabrication building units in Figure 8-3 can be used as well. This selection is arbitrary without any specificity. A photonic band gap has been assembled in Figure 7-3(a). The difference here is that poly(methyl methacrylate) particle does not have satisfactory attractive–repulsive force balance. It is assumed that a repulsive force is dominant over an attractive force so that proper assembly is prevented. In fact, it is not uncommon for colloidal building units to assemble in solution. A well-defined force balance between

attractive and repulsive segments is possible in a rather narrow range of windows. The building unit is chosen, and it cannot assemble in this solution condition. Since directionality is not necessary for this type of photonic band gap device, only assembility is required to have a proper assembly. An external force should bring enough attractive force between poly(methyl methacrylate) particles so that they can assemble through the rebalance of a repulsive force with a forced attractive force. For

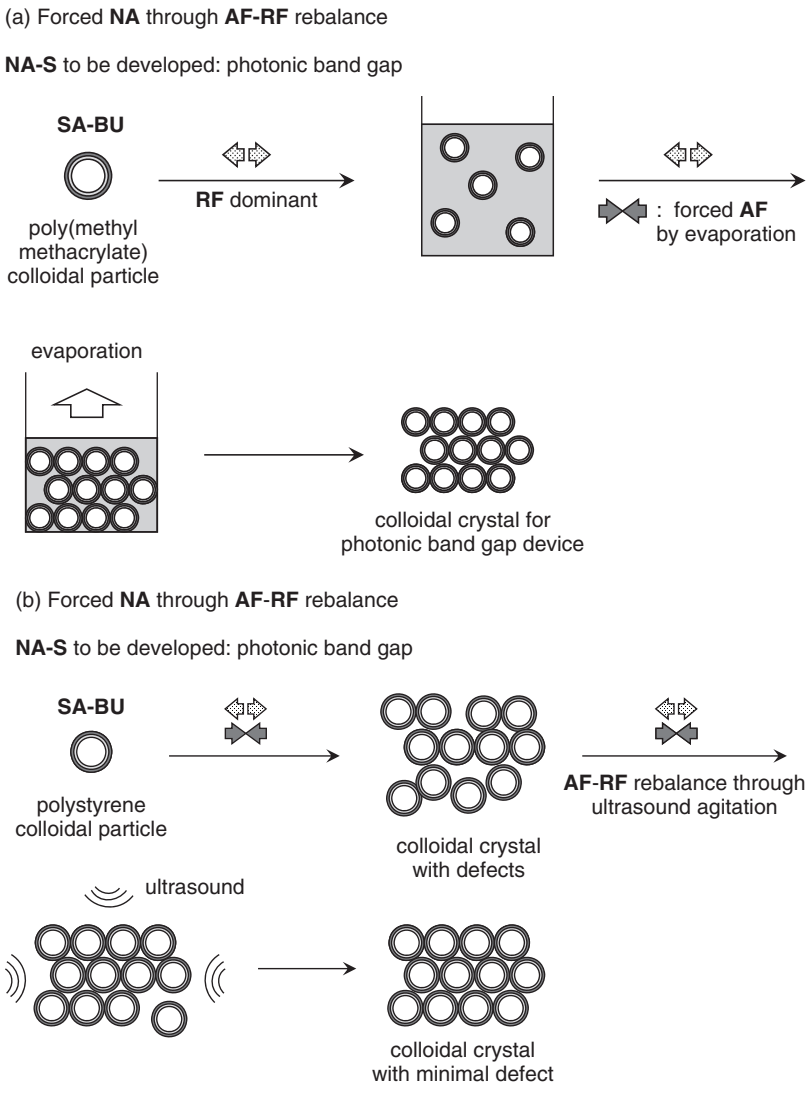

(a) Forced **NA** through **AF-RF** rebalance
NA-S to be developed: photonic band gap
SA-BU
poly(methyl methacrylate) colloidal particle
RF dominant
: forced **AF** by evaporation
evaporation
colloidal crystal for photonic band gap device
(b) Forced **NA** through **AF**-**RF** rebalance
NA-S to be developed: photonic band gap
SA-BU
polystyrene colloidal particle
colloidal crystal with defects
AF-**RF** rebalance through ultrasound agitation
ultrasound
colloidal crystal with minimal defect

Figure 8-4. Forced assembly of nanoassembled systems (**NA-S**): case I. **NA** is short for nanoassembly. **SA-BU** refers to self-assembly building unit. **AF** and **RF** refer to attractive and repulsive forces, respectively.

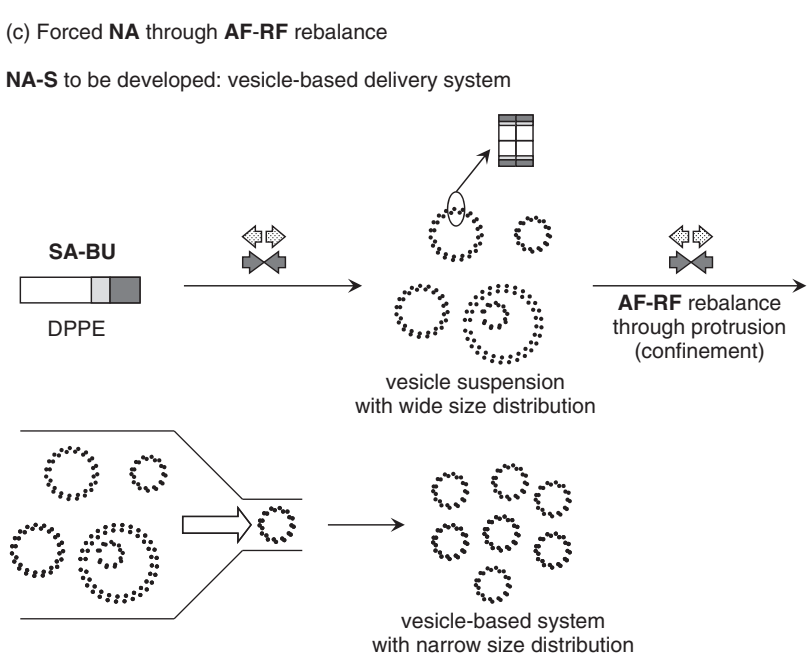


Figure 8-4. (*Continued*)

this specific example, the forced attractive force is generated by evaporation. As the solution evaporates, the number concentration of colloidal particles in solution is increased. This actually can induce more repulsive force between them. However, as evaporation keeps decreasing the average distance between the particles, eventually they will reach the distance where the remaining liquid can provide a capillary force–originated attractive force between them. Evaporation does generate an attractive force, and it is balanced with a repulsive force. The result of this evaporation-induced force rebalance is the colloidal crystal of poly(methyl methacrylate) particles. A characterization of the nanoelement, primarily nanoproperty element, should follow.

For an assembly system like this having a repulsive force–dominant colloidal building unit, the generation of an attractive force can be done by various methods. A centrifugal force–based technique and forced draining of liquid are good examples. This forced assembly is simple and, more importantly, once an external force is identified, there is no need for other additives. Many additives can bring unexpected side effects even though a colloidal crystal with the right structure is obtained. Furthermore, this method can be applied in other modes of assemblies as well.

Case Study 8.1

An actual example can be found in a study that reports the preparation of mesoporous platinum through the self-assembly of nanoparticles with a block

copolymer (Warren et al., 2008). The term *self-assembly* used in this study is the same as *nanoassembly* in terms of the definition given in this book. The platinum nanoparticle whose surface is modified with a ligand, *N,N*-di-2-propoxyethyl-*N*-3-mercaptopropyl-*N*-methylammonium chloride, is the fabrication building unit for this assembly. A preparation of this surface-modified platinum nanoparticle through surface self-assembly was a necessary pre-assembly step to ensure proper assembly with the second building unit, which is the block copolymer. It provides a proper force condition. The block copolymer, poly(isoprene-*block*-dimethylaminoethyl methacrylate), is a self-assembly building unit. Thus, this assembly system has two different types of building unit: one self-assembly building unit and one fabrication building unit. This makes it a heterogeneous system, which in many cases needs the assistance of an external force to archieve a proper rebalance between attractive and repulsive forces. Given the structural analysis of the two building units, repulsive segments are dominant over the attractive segments between them. For the surface-modified platinum nanoparticle, the cationic ammonium group in the shell generates a repulsive force that can overcome van der Waals attractive force. For the block copolymer, there is not enough hydrocarbon chain to induce a strong attractive hydrophobic force. Hence, this is an ideal assembly system that can use a forced assembly. The work indeed used solvent evaporation, which brought a forced additional attractive force between the building units. That way, they were forced to assemble in the form of a nanocomposite with a desired morphology.

Figure 8-4(b) is the second example. Its purpose is also to assemble a colloidal photonic band gap device. The difference from the previous one is its preexisting force balance condition. For this one, it is assumed that polystyrene particles have both attractive and repulsive segments so that they can assemble without any external force. But, as in similar cases of colloidal assembly systems, this polystyrene colloidal crystal that is assembled spontaneously can have noticeable structural defects that can hinder its function. How to minimize structural defects without introducing unnecessary additives is the key point for this example. The building unit is polystyrene particles. Through attractive–repulsive force balance, they can assemble in a given solution condition. Now let us assume that this colloidal crystal shows unacceptable structural defects. Shown in the figure is the use of ultrasound agitation to minimize the defects. Ultrasound applied on the colloidal crystal does not generate any external force–induced directional factor, nor does any forced attractive or repulsive force. However, with proper strength and duration, ultrasound can agitate the colloidal crystal to the extent that it does not destroy the assembility of colloidal crystal but provides an individual colloidal particle room to rearrange within the colloidal crystal. Defect sites usually have more void space than well-assembled sites, which is the result of incomplete force balance between attractive and repulsive segments, usually from kinetic causes. Ultrasound agitation can give individual particles, especially those near or at the defect sites, an instant break from the incomplete force balance and provide the possibility to rebalance through their own attractive and repulsive forces. Once the particles find the right

force balance at the right site, the impact of ultrasound becomes less. This force rebalance will eventually reach the point where the structural defects are minimized. Depending on each assembly system and condition, other external forces can be used as well for the agitation. Mechanical, thermal, and pressure agitations are popular examples. Nanoproperty and nanostructural elements are the main nanoelements to be characterized for this nanoassembled system. Both the structural quality and photonic band gap capability will have to be ensured and correlated.

Case Study 8.2

For more information about the effect of ultrasound on intermolecular and colloidal forces for the self-assembly, refer to Cravotto and Cintas (2009). Their main system of study is hydrogels (sonogels) that are assembled from molecular self-assembly building units. But it clearly shows how ultrasound works to temporarily break the force balance (disassembly) within the self-assembled aggregates and promote reassembly through new force balance. As for many other gel-forming molecular self-assembly building units, the building units in this study mostly have directional and asymmetric packing segments as well. Hence, they are the assembly systems in which these segments participate in the force rebalance process along with the attractive and repulsive segments. All of them have a single type of building unit, which means that, according to Figure 7-1, homogeneous assembly can be effective with either all-at-once or successive mode. Most of the hydrogels can be assembled in one step; thus all-at-once mode is a more effective. A force balance between the building units is already met for the hydrogels. However, since it is considered to have changed without additional building units or additives, they are, according to Figure 8-1, subject to the external force for the force rebalance. The directionality of the gels was not the key issue here. It was accepted as the ultrasound agitation brings to the gels. What was required was the reestablishment of assembility.

The assembly system in Figure 8-4(c) develops a vesicle-based delivery system. The best building unit in Figure 8-3 for the vesicle is 1,2-dipalmitoyl-*L*-α-phosphatidyl ethanolamine. The substance to be delivered is not considered in this example. This makes 1,2-dipalmitoyl-*L*-α-phosphatidyl ethanolamine the only necessary building unit. It has attractive and repulsive segments; thus it should assemble into a vesicle in a proper solution. But there is one critical issue here. The size distribution of the vesicles is important for their applications. However, in many assemblies of lipid vesicles, this is usually not achieved to a satisfactory degree. It almost always is the best option if this can be corrected without any additives. A simple setup for protrusion can provide a fixed confinement for the vesicles. When pushing the vesicle solution through this fixed but controlled space, the vesicles whose sizes are larger than this space face a condition that their initial force balance between attractive and repulsive segments has to be disrupted. And it will be rebalanced during the flow through the passage. The size distribution of vesicles after protrusion will be much narrower than before. 1,2-dipalmitoyl-*L*-α-phosphatidyl ethanolamine also has an asymmetric packing segment. It might have

a somewhat different role depending on the size of the vesicles. But its impact on this force rebalance will be minimal. The vesicles stay stable as long as a repulsive force between them is dominant over an attractive force. The nanostructural element should be properly characterized in order to confirm the size distribution.

8.3.2.2. Directed/Forced Assemblies. Figure 8-5 provides examples of systems that need both assembility and directionality for their reasonable assembly. These comprise case II of Figure 8-2.

The first one is to assemble a nanoassembled system having photonic band gap layer. Figure 8-5(a) is the schematic illustration. Noble metal nanoparticles are an ideal candidate for this. Dodecanethiol-protected silver nanoparticle is shown as a fabrication building unit in Figure 8-3. It has both attractive and repulsive segments. But to assemble the nanoparticles in layered form, there is an absolute need for a substrate, and this often makes them have a segmental situation of repulsive force dominant. Let us assume that this is the situation for this silver nanoparticle and with a given solid substrate. As shown in the figure, nanoparticle solution is placed on the surface of solid substrate first, and the local evaporation of fluid is induced. At or around the area of evaporation, there will be a fluid whose level is decreased and that reaches the point where its height becomes the same or comparable to the size (diameter) of the silver nanoparticle. At this point of evaporation, an immersion capillary force is induced, and it brings the nanoparticles together on the surface of substrate. A convective flow that is also induced by evaporation, but around the area of evaporation, keeps pushing the nanoparticles to the area of evaporation. A simple evaporation thus provides an attractive force for this repulsive force–dominant assembly system. At the same time, evaporation along with substrate generates a directional force that makes the assembled nanoparticles a layered form. External force caused the whole balance between attractive, repulsive, and directional forces acting on the nanoparticles to be rebalanced. If necessary, the assembly can be repeated to assemble additional layers. To confirm the spectroscopic property of this layered system, such as SERS (surface-enhanced Raman scattering), both nanostructural and nanoproperty elements should be primarily characterized.

Case Study 8.3

Assemblies of different birefringent colloidal crystal films are achieved by using optically isotropic spherical colloidal particles (silica and latex particles) (Inasawa and Yamaguchi, 2009). This work demonstrates not only that the assembility of colloidal assembly can be acquired by a simple drying of colloidal suspensions but that its directionality and packing orientation can be controlled as well by simply changing the drying patterns. The origin of the birefringent is the anisotropic packing of the particles, which is directed and forced by the evaporation. Thus, for this particular assembly system, it can be seen that the external force–induced directional factor also acts as an asymmetric packing segment of the colloidal particles.

Case Study 8.4

Another report (Kumnorkaew et al., 2010) confirms that this assembly principle works for a binary colloidal suspension as well. Their assembly system consists of 1 μm (diameter) silica microspheres with 100 nm (diameter) polystyrene nanoparticles. Both of these are self-assembly building units since their surfaces

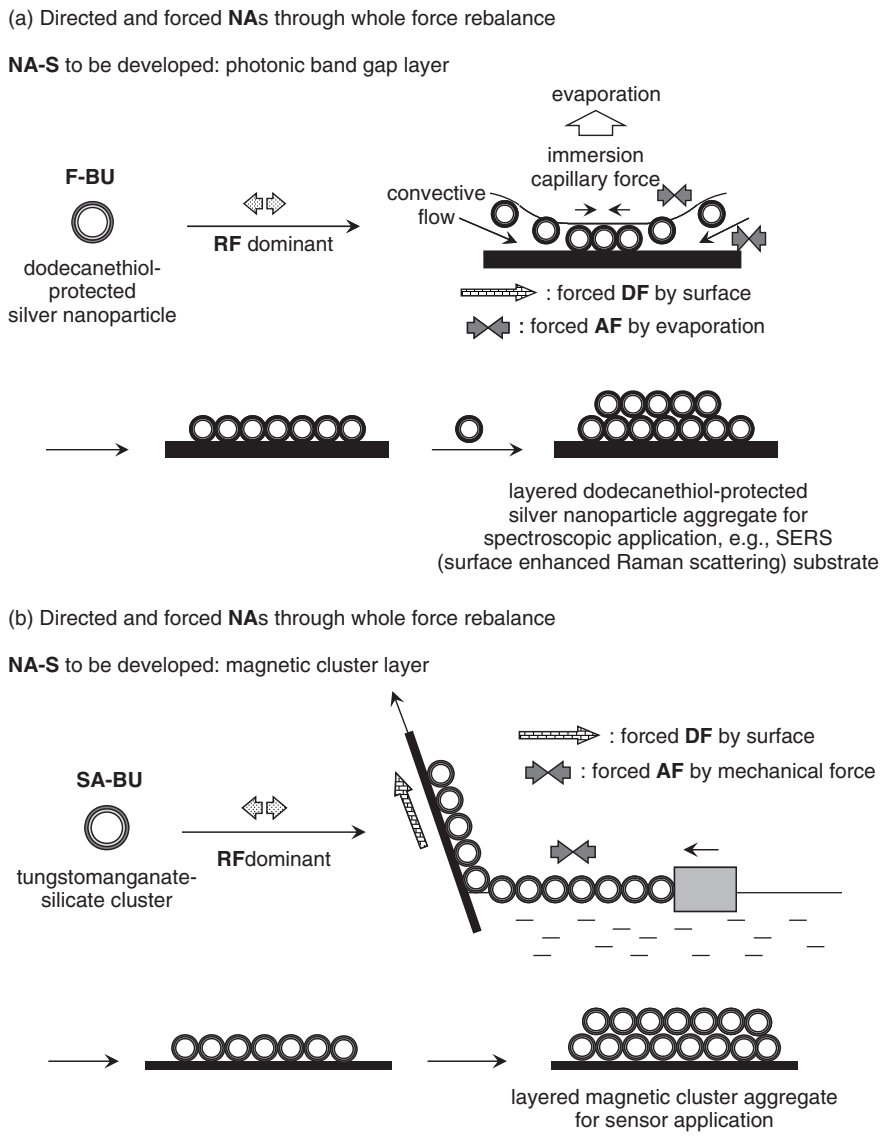


Figure 8-5. Directed and forced assemblies of nanoassembled systems (**NA-S**): case II. **NA** is short for nanoassembly. **SA-BU** and **F-BU** refer to self-assembly and fabrication building units, respectively. **AF, RF**, and **DF** refer to attractive, repulsive, and directional forces, respectively.

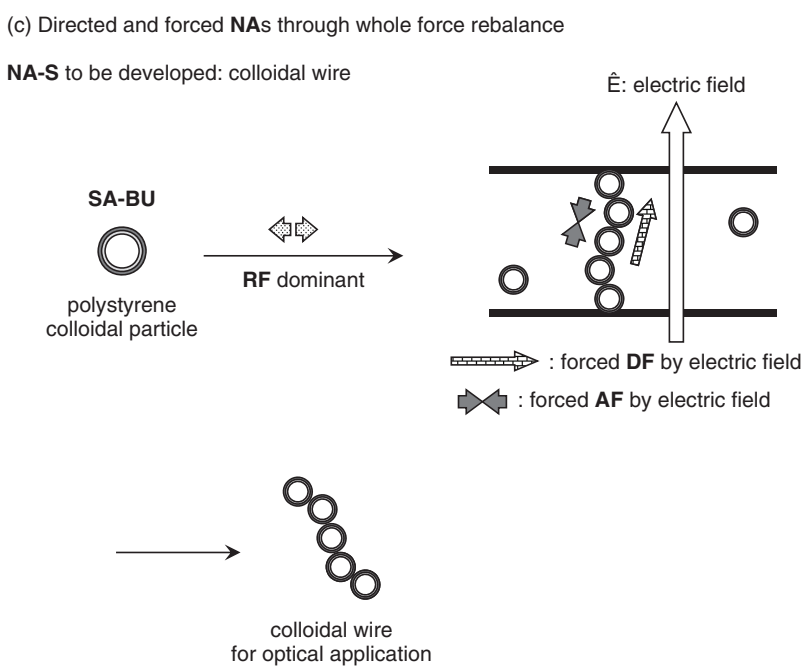


Figure 8-5. (*Continued*)

are not modified with any other building units. Thus, this is an assembly system with single type of building unit. Figure 7-1 illustrates that a homogeneous route with either successive or all-at-once mode is the most effective assembly to select. Given their sizes, van der Waals force is the attractive segment for both of them. And their zeta potential values indicate that their surfaces are highly charged, which means that the electrostatic repulsive force becomes their repulsive segment. The purpose was to build a binary colloidal film. Considering the zeta potential values, the repulsive force between the building units is simply too high to be balanced with van der Waals force. Figures 8-1 and 8-2 say that this assembly can be done only with the aid of proper external force. Assembility is required here. In addition, to assemble them into a film form, directionality has to be generated as well. Hence, this becomes case II of Figure 8-2. A rebalance of all the involved forces is achieved by the convective flow deposition induced by evaporation on the surface of solid substrate. This provided a well-ordered binary colloidal film. An excellent degree of assembility is obtained by this forced assembly and the directionality is provided by the substrate. Careful control of the volume fraction ratio of the building units delicately affected the convective flow, which made all-at-once mode possible for this particular assembly system.

Figure 8-5(b) is to assemble a magnetic cluster layer. Figure 8-3 has tungstomanganatesilicate cluster as a self-assembly building unit. Its unique magnetic property

makes it an ideal building unit for this. It has both attractive and repulsive segments. However, as in the previous example, it often encounters the segmental situation where repulsive force is dominant over an attractive force. This can be the case especially when a given solution promotes higher density of surface charge, which is more likely for this particular cluster. A spontaneous assembly can be problematic. A mechanical force can be a better choice to overcome this strong repulsive force. The Langmuir-Blodgett technique is a well-established method for this purpose. By mechanically pushing the clusters in the direction of solid substrate, an additional attractive force can be imposed on the clusters, which counterbalances the repulsive force. Simultaneous pulling out of the substrate can make the clusters assemble on the surface of the substrate. Both attractive and directional forces are induced by this mechanical external force. And they are rebalanced as a whole, which generates the layered magnetic cluster aggregate. If the condition allows, this process can be repeated to assemble multilayered aggregates. Nanoassembled systems of magnetic clusters can find diverse applications in nanotechnology. For a good example of practical work, see Clemente-Leon et al. (1998).

Figure 8-5(c) shows the assembly of colloidal wire. It is assumed again that this assembly system has a dominant repulsive force over an attractive force. This often becomes the case depending on solution conditions. Polystyrene colloidal particle with its natural surface charge is used as an assembly building unit. Under an electric field with a proper strength and frequency, polystyrene particles in solution can assemble in linear form. The additional attractive force induced by the electric field counterbalances the repulsive force. Furthermore, the electric force can make the particles align in the form of colloidal wire, which means that it promotes a directional force as well. The electric field makes the whole force rebalanced. Colloidal wires can find interesting applications such as in optical devices or as a part of more complicated circuit devices. In terms of segmental structure, a stable electrorheological colloidal suspension implies that a repulsive force between the colloids is dominant over an attractive force. Once it is placed under an electric field with the right strength and frequency, by alternatively turning the electric field on and off, this principle of external force–induced generation of assembility and directionality could yield new application possibilities.

Case Study 8.5

Additional precious knowledge can be acquired, related to this example, by reading an article that reports the formation of colloidal chains and other aggregates through the assembly of polystyrene colloidal particles under ac electric field (Lele et al., 2008). A preparation of electrically functional microwire of gold nanoparticles through forced assembly by using ac electric field also has been reported (Hermanson et al., 2001). This microwire system shows a remarkable electrical property as well as self-repairing and chemical-sensing capabilities. In both reports, there are interesting discussions about the interaction and balance between all the forces involved during the assembly, including the role of external forces.

Case Study 8.6

There is a report on poly(methyl methacrylate) microspheres whose surfaces are modified with hydrocarbon chains assembled under an electric field (Leunissen et al., 2009). This microsphere is a fabrication building unit as shown in Figure 8-3(c). It has both attractive and repulsive segments, which are attributed by van der Waals and steric forces, respectively. However, in this particular assembly system, the solvents closely match the refractive index of the microspheres so that their van der Waals interaction is minimized. Thus, it becomes an assembly system whose building units have dominant repulsive segments. According to Figures 8-1 and 8-2, an external force is needed for their reasonable assembly. The researchers used a biaxial electric field, which generates an inverted dipolar force that counterbalances the steric repulsive force. This indicates that an attractive force is induced by the electric field. And it provides a well-controlled assembility for the system. Furthermore, with this biaxial electric field, they were able to perform an anisotropic control of the assembly, thus generating directionality as well.

8.3.2.3. Directed Assemblies. Case III of Figure 8-2 is for systems whose assembly takes place spontaneously but that need the aid of external forces for better directionality. Figure 8-6 has the details.

Figure 8-6(a) shows the assembly of symmetry-controlled colloidal crystals. Surface alkylated poly(methyl methacrylate) colloidal particle is used as an assembly building unit. This particle has both attractive and repulsive segments. In a proper solution, these two segments can counterbalance each other and so assemble a colloidal crystal. This is a spontaneous process, and the assembly is almost identical to the one in Figure 7-3(b), only with a different building unit. Since this assembly is symmetrical, the colloidal crystal has no specific symmetry, and no specific directionality, either. This can be useful for an application like photonic band gap devices. Now let us assume that there is the possibility of finding improved or novel applications for this, if the symmetry and directionality of the colloidal crystal are varied. This possibility would be even higher if they were controlled with some specific geometry in mind. A self-assembly building unit, Aerosol OT, is used for this control in the figure. In aqueous solution, Aerosol OT can assemble into a typical water-in-oil emulsion that has water droplet inside and oil phase outside. This assembly is through a typical attractive–repulsive force balance between Aerosol OT molecules. If the condition is right with colloidal particles, the water droplet can accommodate the assembly of colloidal particles but only with restricted numbers. It is an assembly in a confinement that is provided by a soft assembled system. The attractive and repulsive segments of colloidal particles are balanced inside the water droplet while the force balance among Aerosol OT molecules sustains its structural integrity. This results in as if the curved surface of emulsion provides a forced directional force. Colloidal crystals with a limited number of particles can be obtained through a careful recovery. The number of

(a) Directed **NA** through **ED** rebalance

NA-S to be developed: symmetry-controlled colloidal crystal

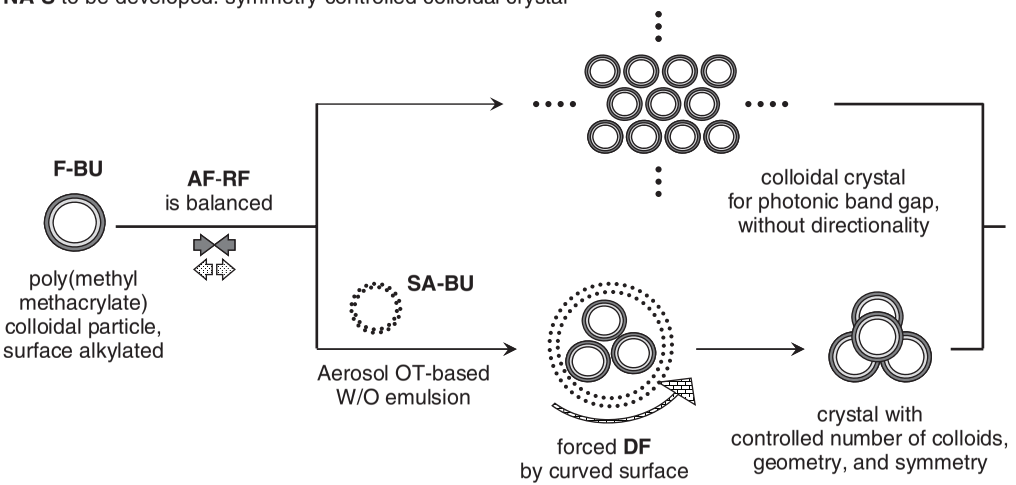
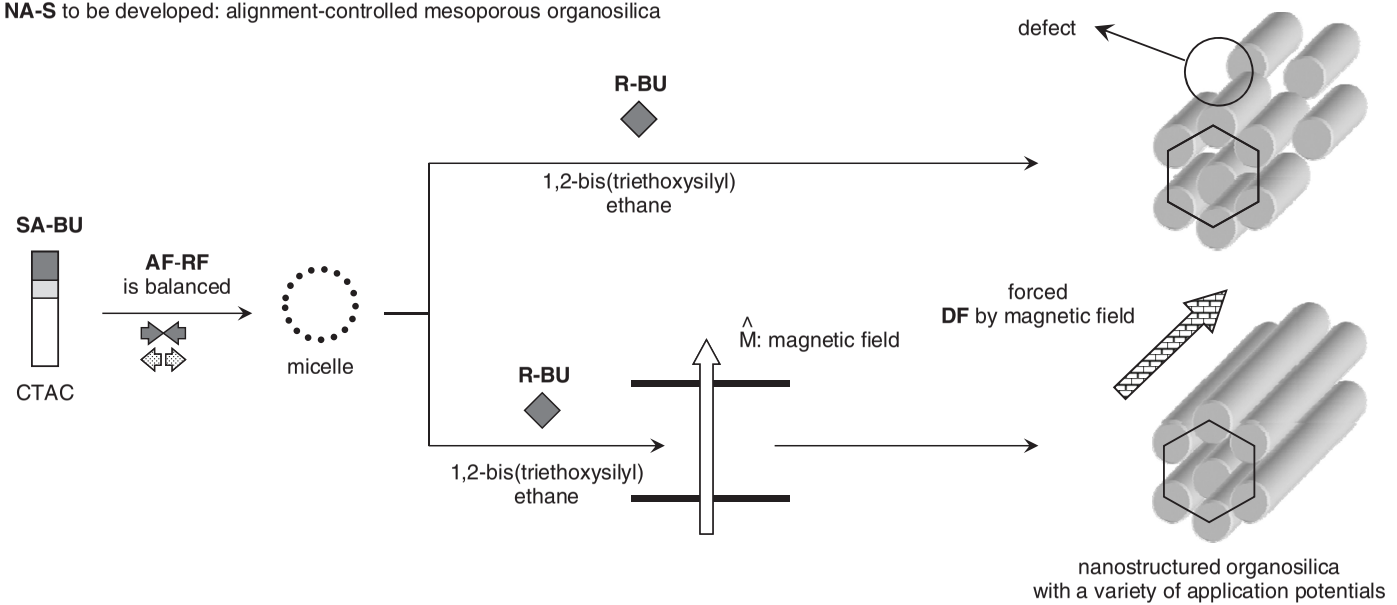


Figure 8-6. Directed assembly of nanoassembled systems (**NA-S**): case III. **NA** is short for nanoassembly. **SA-BU, F-BU**, and **R-BU** refer to self-assembly, fabrication, and reactive building units, respectively. **AF, RF**, and **DF** refer to attractive, repulsive, and directional forces, respectively. **ED** is external force–induced directional factor.

(b) Directed **NA** through **ED** rebalance

NA-S to be developed: alignment-controlled mesoporous organosilica



(c) Directed **NA** through **ED** rebalance

NA-S to be developed: nanostructured titania film

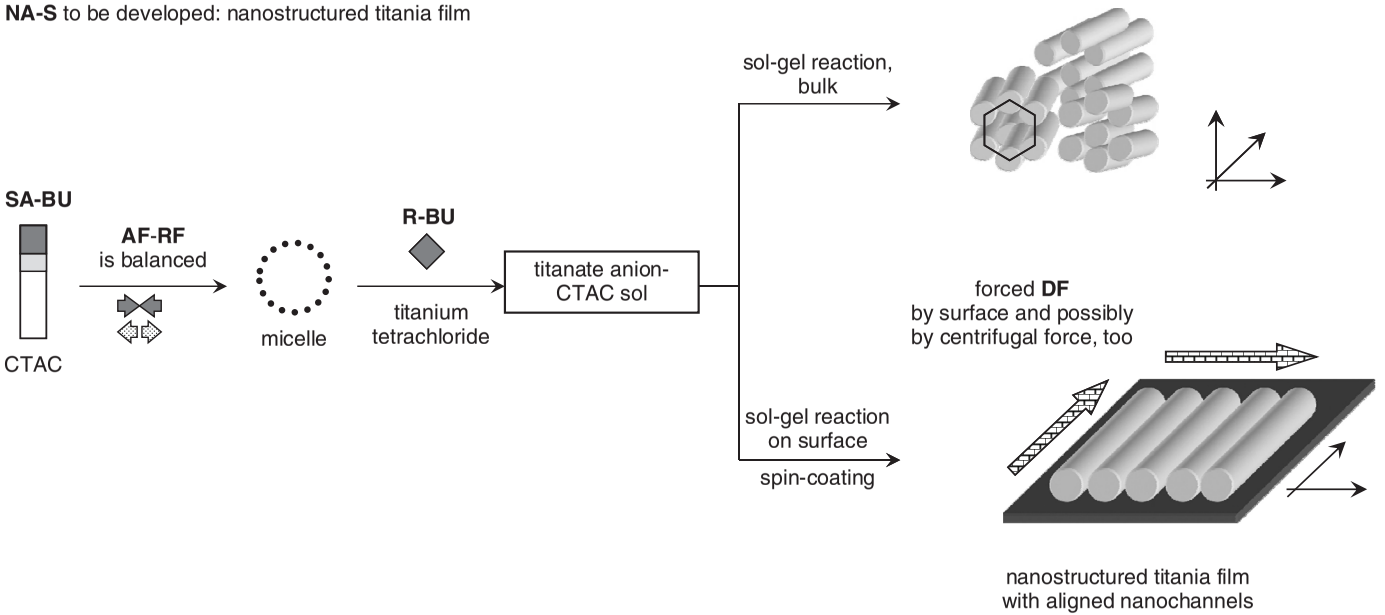


Figure 8-6. (*Continued*)

particles within each colloidal crystal is determined by the size of emulsion. Its overall geometry and symmetry vary by the same factor as well. For this particular system, the segmental structure favored a spontaneous assembly. However, by generating an external force–induced directional factor, the diversity in morphology and symmetry of the colloidal crystals could be controlled. This in turn would expand their application potential. More about this directed colloidal assembly and experimental details can be found at Manoharan et al. (2003).

Let us now consider a mesoporous organosilica that needs a controlled alignment for a certain application. Figure 8-6(b) shows the schematic illustration. The most typical soft self-assembled template for the synthesis of mesoporous inorganic materials is the self-assembled aggregates of surfactant molecules. For better charge matching at the interface between surfactant and inorganic precursor, it is more practical for surfactant to have a head group with its charge opposite to inorganic precursor. Figure 8-3 showed a cationic surfactant, cetyltrimethylammonium chloride. It also showed 1,2-bis(triethoxysilyl) ethane as a reactive building unit. Under the right solution condition, 1,2-bis(triethoxysilyl) ethane can be hydrolyzed first, which generates negatively charged silanol groups as the initial step of this sol-gel process. With the positively charged head group of cetyltrimethylammonium chloride, the charge matching condition becomes ideal for these two building units to assemble mesoporous inorganic material.

The first step of assembly is to have cetyltrimethylammonium chloride micelle. It has both attractive and repulsive segments; thus a typical symmetric force balance induces a spherical micelle whose surface is positively charged. Then, let us assume that we have the sol-gel process of 1,2-bis(triethoxysilyl) ethane in the presence of the cationic micelles but without any external force. In the other set of experiments, let us assume that the same sol-gel process is imposed also in the presence of the cationic micelles but under a magnetic field. For the former assembly, a typical surfactant-precursor (hydrolyzed 1,2-bis(ethoxysilyl) ethane) composite is formed through an electrostatic attraction between the cationic micelle surfaces and anionic precursor species, which is followed by the condensation of the silanol groups. A simple post-treatment to remove the surfactant molecules produces mesoporous organosilica (mesoporous silica whose frame is modified with ethane groups). For the latter assembly, on the other hand, the magnetic field can force the sol-gel process to be aligned in the direction of the field. While the assembled system from the former assembly in reality shows significant structural defects, especially along its long-axis, the organosilica assembled under magnetic field can have an improved long-range alignment. The former assembly takes place spontaneously, and it is often enough to generate a somewhat satisfactory quality of mesoporous organosilica. But by generating an external force–induced directional factor, it was possible to obtain a mesoporous organosilica with better quality, at least in terms of its structural integrity and continuity. Other external forces including flow, electric field, and spatial confinement can also help obtain a better aligned mesoporous organosilica. Control of the orientation of the mesochannels within mesoporous silica film by using air flow provides a good actual example for this directed assembly (Su et al., 2008).

The third example in Figure 8-6(c) is to have nanostructured titania materials with a better structural alignment. As in the previous example, nanostructured titania can be obtained through an electrostatic force balance between self-assembled micelles and oppositely charged precursors. This triggers the sol-gel process. For a titanium source, Figure 8-3 has titanium tetrachloride. For a wide range of solution conditions that will allow its sol-gel process, this reactive building unit can have negatively charged groups. For proper charge matching at the interface with micelles, once again cetyltrimethylammonium chloride will be chosen as the other building unit. It has both attractive and repulsive segments that are balanced symmetrically and thus forms typical cationic micelles. Titanium tetrachloride can now be introduced to this micelle solution, which will generate titanate anion–surfactant sol. Under proper solution conditions, the sol state can be maintained for a considerable period of time. The anionic titanium species are attracted on the surface of cationic micelles, but the condensation can be delayed. For the first set of assemblies, the sol is condensed in bulk. This sol-gel reaction produces a nanostructured composite of surfactant-titania. For the second set, the sol is developed as a film form. A spin-coating or dip-coating method can be performed on solid substrates. While for the first assembly the nanostructured titania would show a good deal of structural defects, the film assembled with the aid of solid substrate can have a better degree of structural alignment. The interaction of the pre-assembled sol with solid substrate generates a directed force along the direction of the surface. If necessary, centrifugal force can be introduced to reinforce this directional force or modify its direction and strength even further. The assembly without solid substrate is spontaneous. It makes a nanostructured titania. But imposing an external force–induced directional factor with solid substrate (and/or centrifugal force) not only allows us to direct its assembly but helps obtain an improved structural quality as well. A careful combination of solid substrate and centrifugal force could induce directional forces in two different ways. A vectorial sum of these forces in a simultaneously or sequentially designed manner could provide a practical means for the control of the detailed structure of this nanoassembled system. Nanostructured titania films with well-aligned nanochannels are in high demand in many nanotechnology fields.

8.3.3. General Assembly Trends under External Forces

Since three different types of building units are involved in nanoassembly (for details, see Sections 2.1 and 2.2), the establishment of its general trends may become complicated compared with those for self-assembly. For the self-assembly, only one type of building units, self-assembly building units, were involved. However, the basic approach is the same as for self-assembly (Figure 2-2). This section shows a general assembly trend for each case in Figure 8-2.

Figure 8-7 is a general overview. The horizontal arrow represents the rebalance of attractive and repulsive forces of nanoassembly building units under external force. It thus is for case I. For case II, its starting point can be anywhere on the arrow

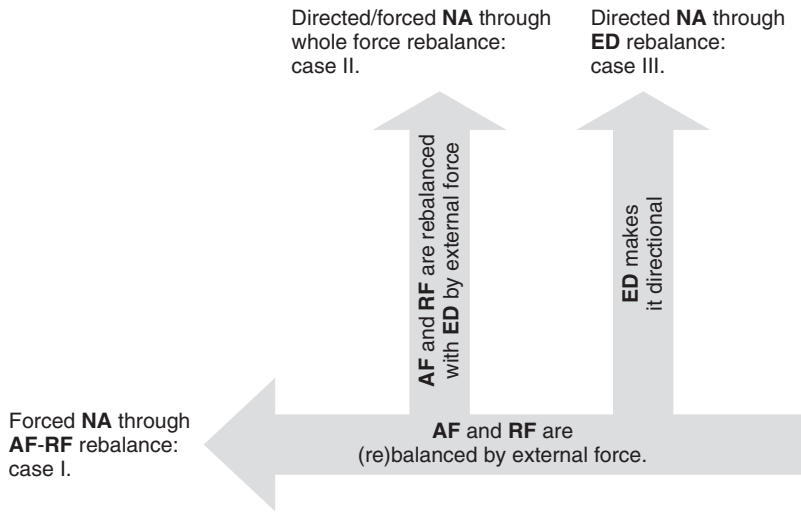

Directed/forced **NA** through whole force rebalance: case II.
Directed **NA** through **ED** rebalance: case III.
AF and **RF** are rebalanced with **ED** by external force
ED makes it directional
Forced **NA** through **AF**-**RF** rebalance: case I.
AF and **RF** are (re)balanced by external force.

Figure 8-7. General trend of directed and forced assemblies. **NA** is short for nanoassembly. **AF** and **RF** refer to attractive and repulsive forces, respectively. **ED** is external force–induced directional factor.

for case I, but its direction is upward, which is represented by the vertical arrow. This is the line representing the rebalance between attractive and repulsive forces with an external force–induced directional factor. Figures 2-5 through 2-8 clarify this. For both cases I and II, the greater the degree of imbalance the segmental structure has, the greater the degree of external force (longer period and/or higher strength) should be used for the generation of satisfactory assembility and/or directionality. For case III, since this is a spontaneous assembly, it can begin from the near-right end of the horizontal arrow. The segmental structure already satisfies the balance between the attractive and repulsive forces. But it should be the role of external force to induce better or new directionality. Greater directionality generally means a greater degree of external force.

8.3.3.1. Forced Assemblies. A general trend for the forced assembly in example (a) of case I (Figure 8-4) is shown in Figure 8-8. It is for the control of photonic band gap through force rebalance. This general trend is similar to the one in Figure 7-7 except that this is under external force. The first option is to change the size of poly(methyl methacrylate) (PMMA) particle. It was the only building unit for this assembly system. The horizontal arrow shows this line of change. The optical absorption gap will then be changed as a function of the size of the particle. The second option, which is represented by the vertical arrow, is to change the distance between the particles. Surface alkylated PMMA particles can be used for this. For each assembly, the sizes of the particles are the same while the distances between them vary almost linearly with a possible upper limit. The optical absorption gap can show a direct correlation with the distances

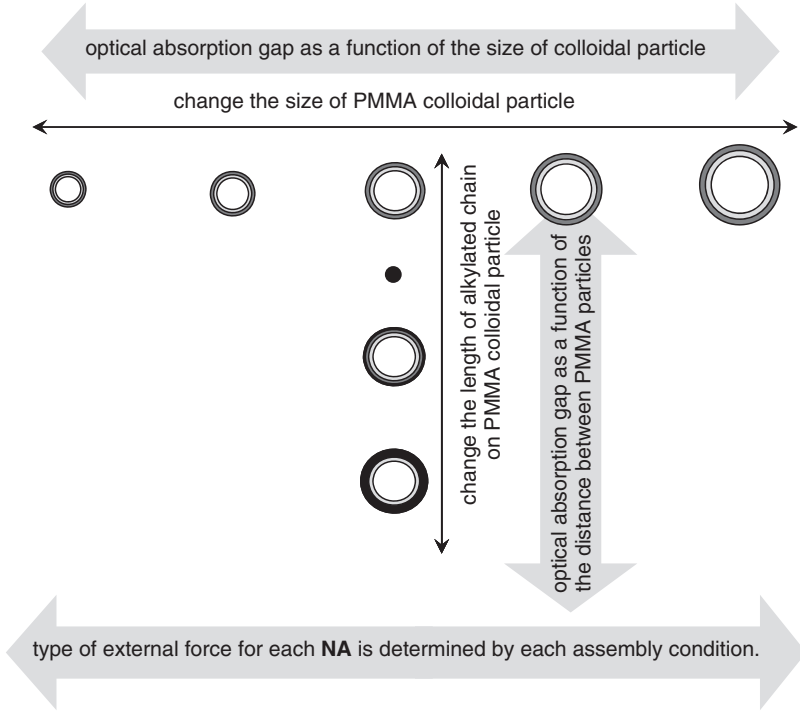

optical absorption gap as a function of the size of colloidal particle
change the size of PMMA colloidal particle
change the length of alkylated chain on PMMA colloidal particle
optical absorption gap as a function of the distance between PMMA particles
type of external force for each NA is determined by each assembly condition.

Figure 8-8. Control of the photonic band (optical absorption) gap via forced assembly: for case I (Figure 8-4(a)). **NA** is short for nanoassembly.

between the particles. This can be applied for different sizes of particles. The type of external force for each assembly system is determined depending on its specific condition. But once a certain external force is selected, simple systematic variation of its condition could be enough to apply it to similar assembly systems.

8.3.3.2. Directed/Forced Assemblies. Figure 8-9 has a general assembly trend for the control of the magnetization of tungstomanganatesilicate cluster film through directed and forced assemblies. This is for example (b) of case II in Figure 8-5. Three distinctive but coupled at some degree options can be drawn for this assembly system. The first one is to control the degree of cluster packing. This can be achieved by controlling the strength of the mechanical force exerted by the mechanical barrier. As shown by the top horizontal thick arrow, the magnetization of the assembled film will be varied as a function of the degree of cluster packing. The second option is displayed on the vertical arrow. It is to change the number of layers within the film. The magnetization of the films is always strongly sensitive on the number of layers. This can be controlled by counting the number of deposition strokes. The third option is to take advantage of additives, if they are acceptable for each application. These can help search

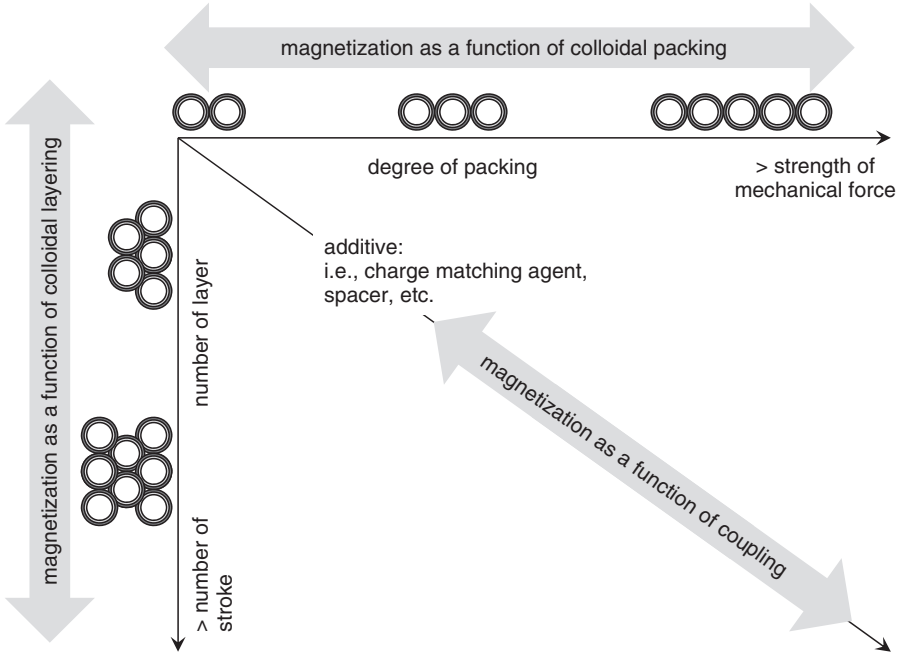

magnetization as a function of colloidal packing
degree of packing
> strength of mechanical force
magnetization as a function of colloidal layering
number of layer
> number of stroke
additive:
i.e., charge matching agent,
spacer, etc.
magnetization as a function of coupling

Figure 8-9. Control of the magnetization of tungstomanganatesilicate cluster film via directed and forced assemblies: for case II (Figure 8-5(b)).

for other functionality. Also, their addition often becomes inevitable in order to ensure that a certain assembly takes place. A spacer that can make the distances between the clusters more accessible is a good example of the former while a charge matching agent is a good example of the latter. Whenever there is an additive, the external force needs enough strength and/or duration that it can overcome a possible force balance conflict caused by the additive. Also, whenever there is an additive, the magnetization of the cluster films will be a function of the coupling with the other two options. The two-dimensional map in the figure could be used like a two-dimensional phase diagram to search for an optimal assembly condition.

8.3.3.3. Directed Assemblies. The unique photocatalytic activity of titania has brought many application possibilities into nanotechnology. Figure 8-10 shows the schematic illustration for the structure control of nanostructured titania films, which is directly related to the degree of their photocatalytic activity. This is a general trend for example (c) of case III in Figure 8-6. This assembly is spontaneous. However, by introducing an external force–induced directional factor, better directionality could be achieved, which can bring a better structural quality and diverse control for them. For this particular assembly system, other options can be used in terms of the improving directionality. It includes the different types of solid substrates, the different rates of solvent evaporation, the different levels of

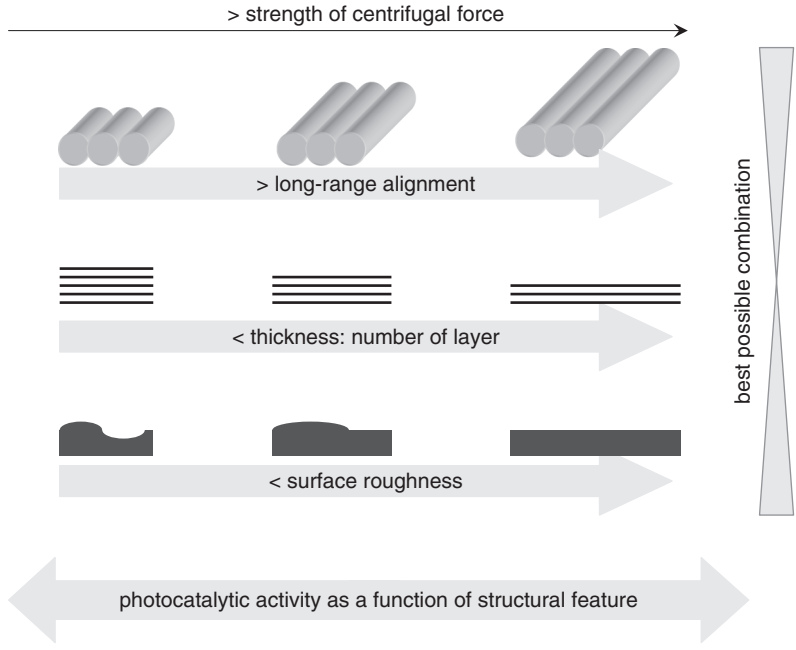

> strength of centrifugal force
> long-range alignment
< thickness: number of layer
< surface roughness
best possible combination
photocatalytic activity as a function of structural feature

Figure 8-10. Control of the structural/catalytic properties of nanostructured titania film via directed assembly: for case III (Figure 8-6(c)).

hydrothermal annealing, and so forth. To be consistent with the example, shown here is the changing of the strength of centrifugal force. As this force that is imposed on solid substrate during the deposition of building units is increased, more directional force is induced. Unless the direction of this directional force directly conflicts with the assembly direction induced by the structural or chemical natures of the solid substrate, the degree of long-range alignment of titania films is enhanced accordingly.

A stronger centrifugal force, on the other hand, can reduce the thickness of the titania films, which means fewer total layers. If the number of building units is controlled along with centrifugal force, the change in the number of layers can be controlled more systematically. Another structural feature that is important for the photocatalytic activity is the surface roughness. When the strength of centrifugal force is increased, the surface roughness is reduced due to the increased directional force. Again, the photocatalytic activity of the titania films is strongly dependent on their structural features. To have the optimum activity, it is necessary to find the optimum combination among these three structural features. This general trend works reasonably as long as the strength of the centrifugal force is within the range where it does not completely disrupt the existing force balance. If the directed force goes beyond this threshold, the assembly system no longer can achieve proper force balance, which means that the assembled system can be broken down. This is the topic of the next subsection.

8.3.3.4. Window of Critical External Forces. The strength of most of the external forces is comparable with intermolecular or colloidal forces. Regardless of their widely different types, this is the most critical point where employing external forces on nanoassembly can be practical. However, for almost all of the external forces, there is a certain window of range where their strengths can be optimal for each assembly system. Figure 8-11 explains the finding (or designing) of the proper window of external forces. A proper window of external force can be located anywhere. It could be at the low end of it, in the middle of it, or at the high end of it. Whatever the actual situation might be, whenever an assembly system is imposed under the external force whose strength is outside of this window, the most likely possibility is that there will be no or poorly developed nanoassembled systems. Below the optimum window, the assembility and/or directionality that are intended to be generated might not be strong enough, while above it they can be too strong to be comparable with building units. The window of external force is unique for each assembly system depending not only on the types of external forces but on the nature of assembly systems as well. Also, depending on similar factors, the boundary of a window can be either critical (sharp boundary) or continuous (smooth boundary). For the former case the impact of external force is more dramatic while the latter case often shows a certain transition state. A wider range of window certainly expands the room to play for nanoassembled systems. Moreover, it could provide the possibility of finding novel nanoassembled systems. The practicality of a sharper or higher barrier of optimum window is almost solely dependent on each assembly system. Sometimes it is the duration of external force that critically determines the success of directed and forced nanoassemblies.

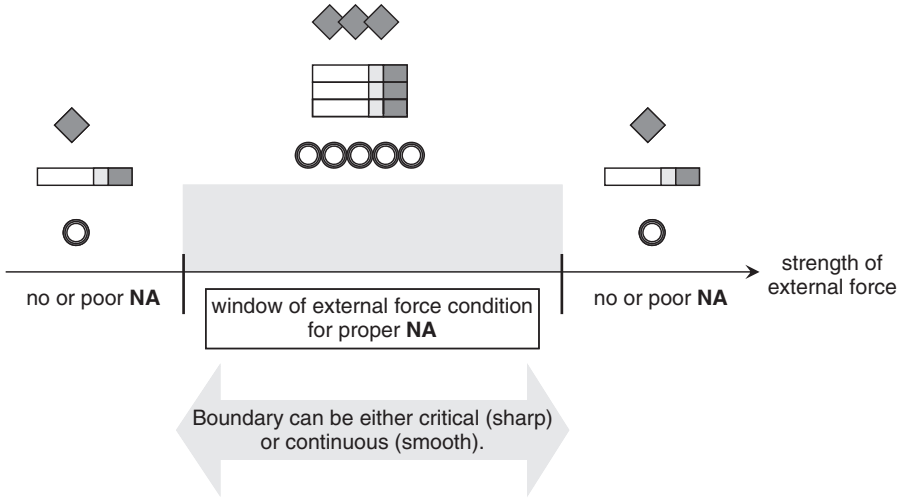

no or poor NA
window of external force condition for proper NA
no or poor NA
strength of external force
Boundary can be either critical (sharp) or continuous (smooth).

Figure 8-11. Finding (or designing) the proper window of external forces for directed and forced assemblies. **NA** is short for nanoassembly.

Case Study 8.7

For an actual example, please see the report about the existence of critical frequency for the assembly of polystyrene particles under electric field (Lele et al., 2008). It also discusses the frequency dependence of the changes in the morphology of self-assembled aggregates. Another example can be found in the literature that shows the effect of the strength and frequency of ac electric field on the assembly of gold nanoparticles into a microwire-based electrode system (Hermanson et al., 2001). The effective assembly is induced only when the field strength exceeds a threshold value. It is equally interesting to observe that there is an optimum range of volume fraction ratio (of small to large building units) for the assembly of well-ordered binary colloidal film (Kumnorkaew et al., 2010). The optimum convective flow for the assembly is induced only when the volume fraction ratio is within the right range.

8.4. TECHNIQUES FOR DIRECTED AND FORCED ASSEMBLIES

Table 8-1 shows various methods that are used for directed and forced nanoassemblies. These are the methods that can improve (or control to some degree) the assembility and/or directionality of a given nanoassembly system. Shown are the most commonly used ones in the literature. The main assembly principles (details in Chapter 7) for each method are also shown. These are not the absolute ones for each method. Rather, these are the ones that are the most practical for each method across diverse assembly systems. The table also shows how the external force–induced directional factor is provided for each method. As with the assembly principles, these are the most practical ones for diverse assembly systems. A main difference of the assembly principles from those in Table 7-1 is this presence of external force during assembly. For example, the vapor-deposited films in Table 7-1 are assembled on surfaces through the homogeneous route. No external forces are involved during the assemblies. The result is nanoassembled systems with a film form. A main parameter to control is their thickness. The role of the surfaces is as simple substrate, and they usually do not become a part of the assembled systems.

On the other hand, the assemblies of the vapor-deposited films in Table 8-1 are directed (often forced) by the specific structural features of the surfaces. The result is assembled systems with specific structural features such as nanopatterns or nanoparticles on surfaces. The role of the surfaces is as external force provider, and they in many cases become a part of the assembled systems. This table shows only surface epitaxy and defects. (Table 8-2 in the next section has more details of various directional factors generated by different surfaces.) Whenever one of the methods in Table 8-1 is used in the literature, these assembly principles can be a handy guide to track the mechanistic processes and the origin of the nanostructures and corresponding nanoproperties.

TABLE 8-1. Collection of various methods used for directed and forced assemblies, and their relation to main assembly principles. Surface and solution indicate assemblies on surface and in solution, respectively. ho, he, and ch refer to homogeneous, heterogeneous, and chiral assemblies, respectively. ED is external force–induced directional factor.

Method	Assembly Principle	**ED** Provided By
Langmuir-Blodgett deposition	surface: ho, he	surface/mechanical force
Langmuir-Shafer deposition	surface: ho, he	surface/mechanical force
layer-by-layer coating	surface: ho, he	surface
spin-coating	surface/solution: ho, he	surface/centrifugal force
dip-coating	surface/solution: ho, he	surface/gravity
electrospinning	surface/solution: ho, he	surface/electrochem.
electrodeposition	surface/solution: ho, he	surface/electrochem.
CVD (chemical vapor deposition)	surface: ho	surface epitaxy/defects
MOCVD (metalorganic CVD)	surface: ho	surface epitaxy/defects
PECVD (plasma-enhanced CVD)	surface: ho	surface epitaxy/defects
ion-plating vapor deposited film	surface: ho	surface epitaxy/defects
physical vapor deposited film	surface: ho	surface epitaxy/defects
laser ablation vapor deposited film	surface: ho	surface epitaxy/defects
photochemical vapor deposited film	surface: ho	surface epitaxy/defects
controlled evaporation	solution: ho	convective flow
assembly in nanochannel	solution: ho, he, ch	capillary force

8.5. SURFACE-INDUCED DIRECTED AND FORCED ASSEMBLIES

Table 8-2 shows various structural features of surfaces that can promote directed and forced assemblies on surfaces. The ones that are well-studied, both experimentally and theoretically, in a wide range of different reports are collected in the table. Quite remarkably, for almost of all of them, their structural features and their structural boundaries are within the nanometer scale. This is the most critical point that makes directed and forced nanoassemblies possible on diverse surfaces, because they not only provide assembility and directionality for a given assembly system, but determine the nanoscale structural features of the assembled system as well. This eventually determines nanoproperties. Also, while there are many directed and forced assemblies taking place in solution, the majority of these assemblies that are practical occur on surfaces. This is another point that is made by collecting only surface-induced directional factors in the table. Usually, solid surfaces work better as external force providers. But some of the soft surfaces work fine as well. Self-assembled monolayers, physisorbed monolayers, multilayers, and liquid surfaces under certain conditions are good examples.

8.6. COLLECTION OF NANOASSEMBLED SYSTEMS II

Table 8-3 collects the nanoassembled systems that are obtained via directed and forced assemblies and frequently appear in the literature. Their assemblies always take place under an external force or under combined external forces. The assembled systems shown in Section 7.4 (Table 7-1) were those that are assembled

TABLE 8-2. Collection of external force–induced directional factors (ED) that can be generated by surfaces.

Directional Factor	Surface Type
epitaxial matching	solid
herringbone reconstruction	solid
vicinal surface	solid
nanoisland	solid
spiral surface defect	solid
surface mismatch	solid
surface symmetry	solid (mostly metal)
step edge	solid
surface stress	solid
strain-relief pattern	solid
surface dislocation	solid
local fluctuation	liquid
compositional gradient	self-assembled monolayer on solid surfaces
controlled surface energy	self-assembled monolayer/film/nanostructure on solid surfaces

TABLE 8-3. Collection of nanoassembled systems that are obtained via directed and forced assemblies.

Nanoassemblded System	Assembly Mainly On/In
atomic wires	solid surface
molecular wires	solid surface
colloidal wires (chains)	solid surface, solution
colloidal crystal layers	solid surface
spin-, dip-coated films	solid surface
nanoparticles and nanoclusters	solid surface, liquid surface, solution
nanorods and nanowires	solid surface, liquid surface, solution
nanofilms	solid surface, liquid surface
hierarchical nanostructures	solid surface, liquid surface, solution
controlled precipitates: e.g., Liesegang rings	solution
biominerals	solution

spontaneously without any external forces. The media where the assembly usually occurs are also shown. A general understanding about them can be useful. For example, atomic and molecular wires are almost exclusively assembled on surfaces. This is because, since the building units for them are quite small, the generation of linear directionality (which is necessary for the wire type of assembled systems) in solutions is usually disrupted by their Brownian motion. On surfaces, the attraction between the building units and surfaces significantly reduces the degree of the freedom of the building units, which can make the generation of the necessary linear directionality more favorable than in solution. On the other hand, colloidal wires whose building units are much bigger and heavier than the molecular building units can be assembled both on surfaces and in solution, whenever the external forces are well-selected and controlled. For another example, almost of all of the nanoparticles and nanoclusters are assembled from their precursors within the spatial confinement provided by directional factors such as surface structural

features and self-assembled aggregates. Without the directional factors, they usually cannot express the nanoscale structures and often the assembly itself is not possible.

Most of the nanoassembled systems in Table 7-1 can be assembled also under external forces, but it is rare that those in Table 8-3 are formed without taking directed or forced assembly routes. This suggests that, when one of the assembled systems in Table 8-3 has a key purpose for a certain assembly system, it is critical to identify the role of the external force and how it is changing the assembility and directionality of the system. The relationship of the parameters of the external force to the structure and property of the assembled system can be better understood this way.

8.7. SUMMARY

Directed and forced assemblies bring various physical forces to nanoassembly. The main issue in this chapter was how to effectively apply them so that the general outcome of nanoassembly can be improved. It showed that:

1. External forces can be used for a wide range of different types and kinds of building units.
2. Their roles in the assembly can be understood based on the force balance with the building units.
3. This is because the interactions of external forces with the building units are comparable to the interactions among the building units.
4. A well-controlled external force can provide assembility and directionality for assembly systems that otherwise lack them.
5. It can also provide some degree of directionality for spontaneous assembly systems.
6. By including external forces in a nanoassembly, it is possible to expand the scope of its building units, which in turn can diversify the assembled systems.

Finally, whenever directed and forced assemblies are taken, it is highly likely that the assembled systems are stabilized kinetically. Thus, how we manage the kinetic nature of the assembly processes can make a significant difference in the nature of the assembled systems.

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Part III

Applications

9

External Signal–Responsive Nanomaterials

9.1. NANOISSUE

The second part of the book presented six main assembly principles for the design of self-assembling nanotechnology systems. It began with the identification of self-assembly capability followed by the multi-step self-assembly. The structural determination of self-assembled aggregates and the control of their hierarchy and chirality were the next two. The final two were assemblies with multiple building units and directed/forced assemblies. Both of these were assemblies expanded from self-assembly (*nanoassembly*; see Section 2.1 for details). All of these issues were approached based on segmental analysis (unified structural analysis of assembly building units; see Subsection 1.2.2 for details). And all of the assembly segments were intrinsic. In other words, the answers to these issues were already incorporated into the individual assembly building units.

There is a special group of assembly building units whose specific part (segment) exclusively responds to a specific signal from outside the assembly system. The pattern of response by the building units is diverse depending on the individual systems. It can be structural, compositional, conformational, reactional, or polarizational. This segment is called *external force–specific functional segment*. (See Subsection 1.2.2.2 for details; Table 1-13 collects the self-assembly building units with this segment.) The third part of the book presents the applications of self-assembled nanotechnology systems. This first chapter of Part III addresses how this special group of assembly units works and how it is applied to the

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development of nanotechnology systems, specifically in the development of external signal–responsive nanomaterials. This issue itself has an important implication for nanotechnology. In addition, it provides some basic principles for the issues of the following chapters.

The term *external signal* here is basically the same as the term *external force* in Chapter 8. It is also called *external field* and *external stimulus*. What is different from Chapter 8 is how it interacts with the building units. For the directed/forced assemblies in Chapter 8, the external signal acts on entire building units, thereby changing the whole interactions between them. It thus is non-site specific. For this chapter, however, the external signal is effective mainly on the external force–specific functional segment of each building unit. It thus is site specific, which actually makes the key point for the development of external signal–responsive nanomaterials. The driving forces for the assemblies in both chapters are comparable to external signals in terms of their strengths and interacting ranges. Hence, the main issue to be described in this chapter is:

Does your assembly system respond site-specifically to a given external signal?

If so,

What are the key assembly principles?

and

How can it be assembled into the nanomaterials that respond to external signals?

Typical external signals include ultraviolet, visible light, laser light, microwave, solution pH, flow, temperature, pressure, magnetic field, electric filed, ultrasound, and so forth. The detailed nature of external signals and their working principles in self-assembly systems were discussed elsewhere (Lee, 2008).

9.2. GENERAL OVERVIEW

Once again, external signals can affect the segments of assembly building units independently depending on the conditions. They can also affect the entire building unit as a whole. For both cases, this is when the "external force–induced directional factor" (details in Figure 1-5) comes into the scheme of force balance. For the site-specificity of external signals, the external force–specific functional segment is defined (details also in Figure 1-5).

Figure 9-1 presents a general overview to determine the impact of external signals on the nanoassembly with external signal–responsive building unit. Nanoassembly is an assembly with different types and kinds of building units (for details, see Section 2.1), and includes self-assembly (for details, see Section 2.6). External signal–responsive building units are any types and kinds of building units that have at least one external force–specific functional segment. For the sake

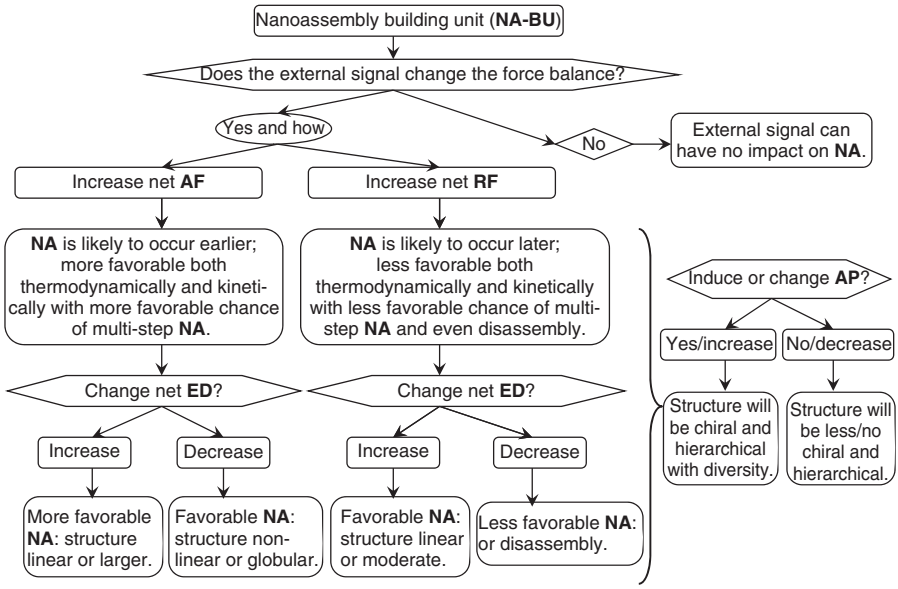
Nanoassembly building unit (NA-BU)
Does the external signal change the force balance?
Yes and how
No
External signal can have no impact on NA.
Increase net AF
Increase net RF
NA is likely to occur earlier; more favorable both thermodynamically and kinetically with more favorable chance of multi-step NA.
NA is likely to occur later; less favorable both thermodynamically and kinetically with less favorable chance of multi-step NA and even disassembly.
Induce or change AP?
Yes/increase
No/decrease
Structure will be chiral and hierarchical with diversity.
Structure will be less/no chiral and hierarchical.
Change net ED?
Change net ED?
Increase
Decrease
Increase
Decrease
More favorable NA: structure linear or larger.
Favorable NA: structure non-linear or globular.
Favorable NA: structure linear or moderate.
Less favorable NA: or disassembly.

Figure 9-1. General overview of the nanoassembly with external signal–responsive building units. **NA** is short for nanoassembly. **AF** and **RF** refer to attractive and repulsive forces, respectively. **AP** is asymmetric packing segment. **ED** is external force–induced directional factor.

of simplicity, the role of this segment is not included in the diagram. Detailed examples will be shown throughout the chapter.

The first question to ask is whether the external signal affects any of the segments within the building unit. If the answer to this question is no, then the external signal can be assumed to have no or negligible impact on the assembly of that particular building unit. If, however, the answer is yes, then the next question to ask is whether the vectorial sum of the external signal increases the net repulsive force between the building units or increases the net attractive force between them. (Usually, an impact of the external signal on the individual building unit is not monotonic. It comes with different degrees of magnitude and is constantly varied depending on its dynamic position. This is why the term *vectorial sum* is more practical to express its true impact.) A decreasing of the repulsive force could imply the increasing of the attractive force while decreasing attractive force could correspond to increasing repulsive force.

If the answer to this second question is yes, that the external signal increases the net repulsive force, then the assembly is likely to occur later compared with the assembly without it. "Later" here means that the assembly becomes less favorable both thermodynamically and kinetically. This is simply because there is greater repulsive force that counterbalances the attractive force. In addition, this condition makes the chance of multi-step assembly less likely or reduces the order of the existing multi-step assembly. For an extreme degree of external signal, it is not uncommon that the assembly does not take place at all or the aggregates that are

formed prior to the introduction of the external signal are pushed toward the process of disassembly. The third question is how the external signal changes the external force–induced directional factor. This factor is different from the directional segment of the building units (details in Figure 1-3). A directional segment is a part of the building units, thus is intrinsic. The external force–induced directional factor is induced by external signals, thus is extrinsic. The way they act on the building unit is different, too. The directional segment solely interacts with the directional segments from the neighboring building units. On the other hand, the external force–induced directional factor works either on a specific part of the building unit or on the whole building unit. The results from these two directional forces can be similar, but they can also make the outcome of the assembly markedly different. Whatever the actual situation might be, if it decreases the net directional force, it is likely that the assembly becomes less favorable with reduced capability of multi-step assembly. There is even a possibility that the aggregates disassemble. If the answer, however, is that it increases the directional force, the outcome becomes the opposite. The assembly should be favorable with a high possibility of multi-step assembly. The directional force likely promotes the aggregates to be a linear type of morphology.

If the answer to the second question is yes, that the external signal increases the net attractive force, the assembly should be more favorable than the one without the external signal. The assembly should occur earlier whether it is driven thermodynamically or kinetically. Capability of multi-step assembly should increase, too. Simply speaking, there is more attractive force than before while the repulsive force is either the same or decreased. The next question asks how the external signal changes the net external force–induced directional factor. If it decreases the directional force, it is still likely that the assembly becomes favorable. Compared with the previous case that increases the net repulsive force, there is more attractive force. Capability of multi-step assembly is still high. And, the lack of directional force makes it highly probable that the aggregates have nonlinear or globular types of morphologies. If, on the other hand, the external signal increases this factor, the assembly should be more favorable than all the others. The same should go for the capability of multi-step assembly. A high degree of directional force induces the aggregates to have a linear type of morphology.

As briefly described in the previous chapter, external signals often have significant impact on an asymmetric packing of the building units. They can promote asymmetric packing even with the building units that do not have any asymmetric packing segment. They can also reduce it. The diagram on the right-hand side shows this aspect. Whether the external signal increases the net attractive or repulsive force, its impact on asymmetric packing can be expressed with this simple diagram. When the external signal has no impact or works to decrease the degree of the asymmetric packing, the morphology of the aggregates is changed a little or expressed less than the one that can be fully induced by the asymmetric packing. This means that the chirality and hierarchy of the aggregates could be reduced or might not appear at all. If the external signal enhances the asymmetric packing, the impact on the aggregates becomes the opposite. The aggregates should

have strongly expressed chirality and hierarchy, which in turn brings more diverse structures.

9.3. ASSEMBLY PRINCIPLES

9.3.1. External Signal–Responsive Molecular Assemblies

Figure 9-2 shows the schematic illustration for the effect of external signals on nanoassembly systems consisting of external signal–responsive molecular building units. The symbols representing each segment come from Figures 1-3 and 1-5. An external force–specific functional segment is included, and an external force–induced directional factor is treated as an outside factor. An asymmetric packing segment is not included.

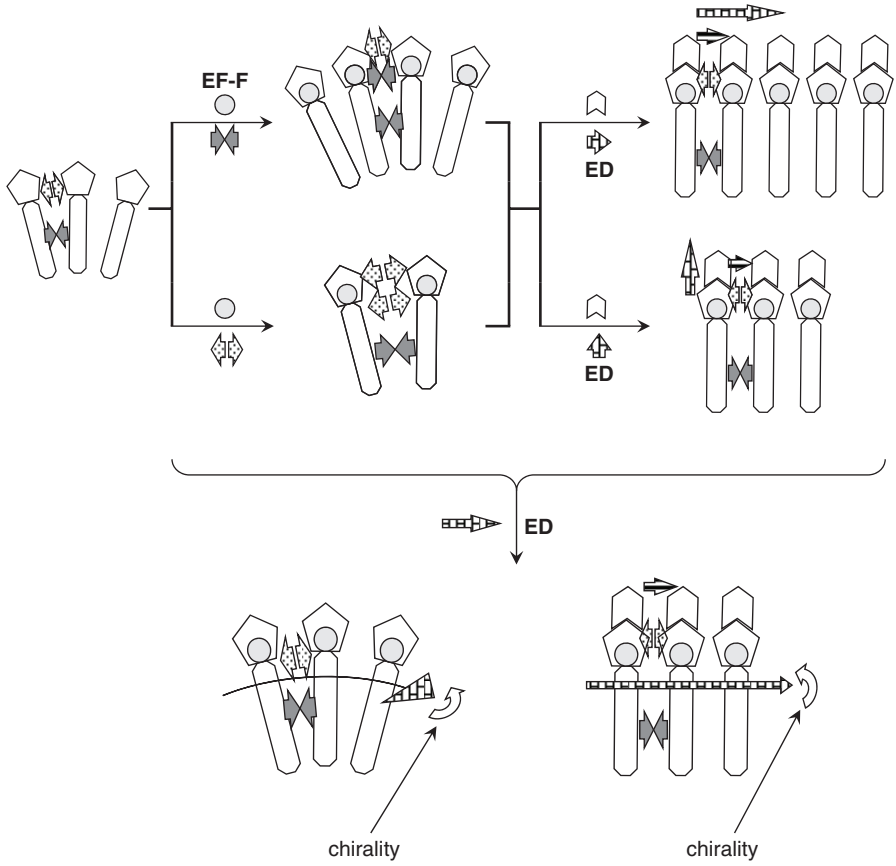

Figure 9-2. Schematic explanation of the nanoassembly with external signal–responsive molecular building units. **EF-F** refers to external force–specific functional segment. **ED** is external force–induced directional factor.

First, let us assume that we have a self-assembly building unit with the most basic segmental structure. It is composed of one attractive segment and one repulsive segment. (Table 1-4 lists the self-assembly building units having this type of segmental structure.) The segmental interaction is symmetric. Next, let us add an external force–specific functional segment. For this scheme, it is added within the repulsive segment, but for actual assembly systems, the location of this segment can be anywhere within the building units. The scenarios for the next step can be divided into two: the external force–specific functional segment can add an attractive force to the attractive segment, or it can add a repulsive force to the repulsive segment. A simple segmental analysis can say that, for the former case, the assembly will be favored in this step while, for the latter case, the assembly should be less favorable compared with the one without the external force–specific functional segment. Meanwhile, the role of the external force–induced directional factor can be expressed in two extreme ways for both cases of the previous step. The first is the case when this factor works with the directional segment cooperatively. The second is when it works against the directional segment. For the former case, the directionality of the assembly is reinforced and the aggregates show a linear type of morphology. It becomes the opposite for the latter case. The directionality of the assembly induced by the directional segment is disrupted and the result is a less directional assembly. The aggregates have a globular or nonlinear type of morphology. For most assembly systems in reality, the assembly configuration will be in between these two extreme scenarios. And their outcome will be decided by what the vectorial sum of the two directional forces turns out to be. The bold-lined arrow is for the directional force between the directional segments and the block-patterned arrow is for the external force–induced directional factor. As shown in Figure 9-1, the external force–induced directional factor can induce an asymmetric packing even on building units that have no asymmetric packing segment. The scheme at the bottom shows this aspect. Chirality is indicated with the curved arrow. For some related insights about the design of the interactions between the building units and the control of assembly conditions, refer to a review by Weiss (2008).

9.3.1.1. Light-Responsive Assemblies. The azobenzene group is a well-known light-sensitive group. The first example of the section is a self-assembly building unit with this azobenzene group. Figure 9-3(a) shows its molecular structure and the segmental analysis based on it. Figure 9-3(b) depicts the response by its assembled systems to light. The condition is assumed to be at room temperature in water.

The one on the left-hand side of Figure 9-3(a) is the *trans*-form of this building unit and the one on the right-hand side is the *cis*-form. Its conformational change is triggered by the irradiation of ultraviolet and visible light. It is well known that the azo-part is solely responsible for this change. Hence, it is clear that the azo-part should be assigned as an external force–specific functional segment for both forms. The heptyl hydrocarbon chains attached with the phenoxy group on both sides of the azo-part are assigned as their attractive segment. The heptyl hydrocarbon chain

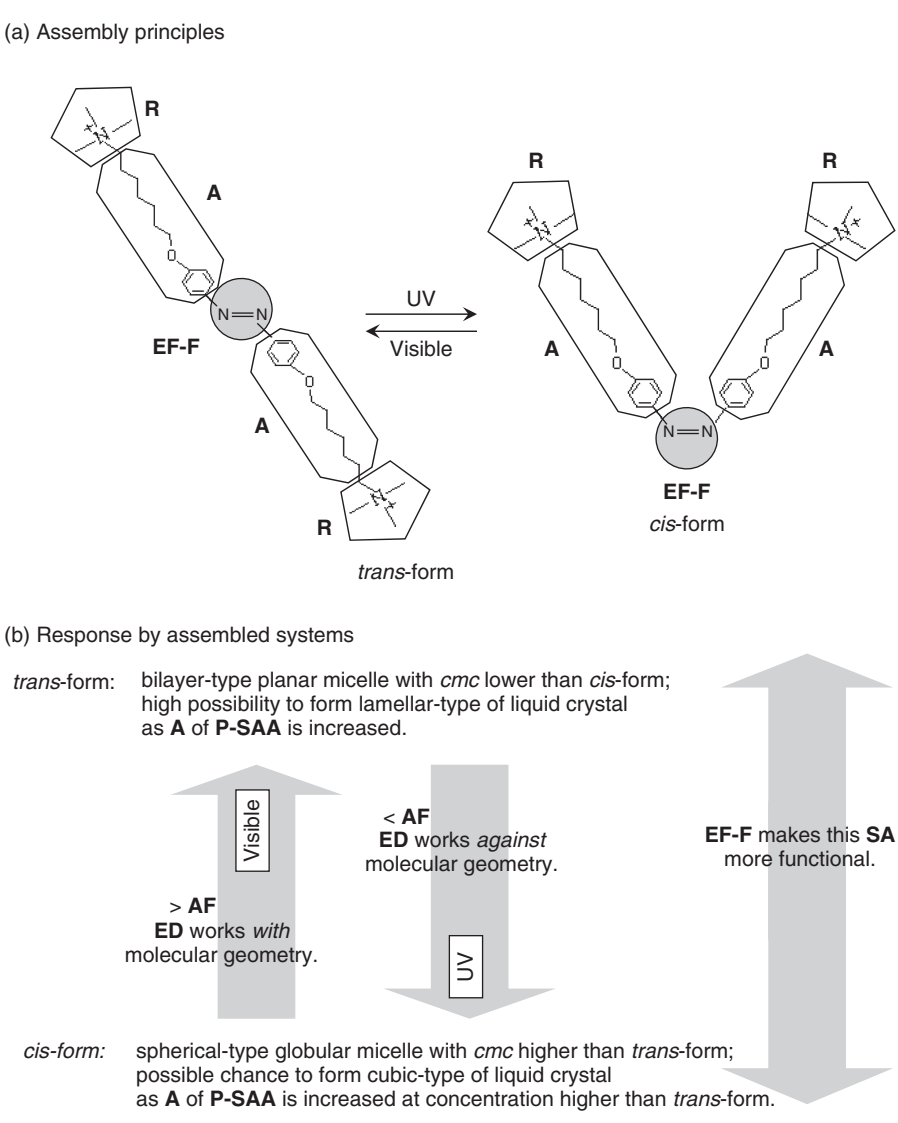

Figure 9-3. Light-responsive molecular self-assembly. **A, R**, and **EF-F** refer to attractive, repulsive, and external force–specific functional segments, respectively. **AF** is attractive force. **ED** is external force–induced directional factor. **SA** and **P-SAA** are short for self-assembly and primary self-assembled aggregate, respectively. *cmc* is critical micellar concentration.

is long enough so that it can generate an attractive hydrophobic force between them. The phenoxy group might disrupt the attractive force of the heptyl chain, but the geometry of the azo-part that will determine the alignment of the phenoxy group will make its configuration not much out-of-the plane, in other words, close to side-by-side mode. This makes it induce mainly $\pi-\pi$ attractive interaction. It

thus is reasonable to assign the phenoxy group as a part of the attractive segment. A benzene ring–based group is one of the common directional segments. The phenoxy group in this building unit certainly has some degree of directional force, but because of this geometrical constraint, the degree of this directional force becomes quite low. This is why the phenoxy group is not assigned as a directional segment here. This assignment is valid for both forms. A repulsive segment is straightforward. It is the two trimethylammonium groups on both ends of the building unit. The positively charged nitrogen atoms generate an electrostatic repulsive force between them. Both forms of the building unit have two fundamental (attractive and repulsive) segments with one external force–specific functional segment.

Figure 9-3(b) explains how the assembled systems of this building unit respond to light. Let us begin with the *trans*-form. Its molecular configuration is close to linear. And it has an identical repulsive segment on both ends with two identical attractive segments in between. This allows us to view it as if it were a *bola*-form amphiphile. The two attractive segments bring the building units together as if they worked as one long hydrocarbon chain. And the repulsive segments counterbalance it. This analysis provides a high chance of forming bilayer-type of planar self-assembled aggregates (or micelle). The *cmc* (critical micellar concentration) should be much lower than that of the *cis*-form because of its stronger attractive interaction than the *cis*-form. When the condition favors higher-order assembly (as the attractive force of the primary aggregates is increased), it is most likely that the higher-order aggregates become a lamellar type of liquid crystal. Now let us assume that ultraviolet is irradiated on the *trans*-form or on its aggregate. The external force–specific functional segment changes its configuration to *cis*-form, which in turn changes the entire configuration of the building unit into *cis*-form as well. This induces a reduced attractive force for the *cis*-form compared with the *trans*-form. For the *trans*-form, when two building units are interacting, the two attractive segments can have a full degree of attractive interaction. This means that all attractive segments are in full contact during the assembly. But for the *cis*-form, its geometrical character fixes the positions of the two attractive segments so that they maintain a certain distance of a certain degree from the external force–specific functional segment. This geometrical constraint reduces the degree of the attractive interaction roughly by half compared with the *trans*-form. Furthermore, this segmental analysis can be interpreted as the external force–induced directional factor working *against* the molecular geometry of the building unit. The external signal works toward the opposite direction against the initial packing that is favored by the molecular geometry. A change in segmental structure that reduces an attractive force guarantees a less favorable assembly. The *cis*-form has a high chance of forming a spherical type of globular micelle with its *cmc* value much higher than the one of *trans*-form. If the condition favors higher-order assembly, its aggregates would be close to a cubic type of liquid crystal. When visible light is irradiated on the *cis*-form or on its aggregate, the assembly and its outcome become the opposite. The molecular geometry becomes more attractive interaction friendly. The external force–induced directional factor now works *with*

the molecular geometry. As long as the molecular integrity of this building unit is maintained, this functional assembly can be continued reversibly. It is the external force–specific functional segment that works as the key component to make this assembly system a functional one.

9.3.1.2. Catalytic Reaction–Responsive Assemblies. This is for the assembly system whose building unit responds to a catalytic reaction. Figure 9-4 shows the assembly principles and the response by the assembled systems. The condition is at room temperature in water.

This building unit has exactly the same two undecyltrimethylammonium groups that are attached on a disulfide group. This gives the name *bis*-form. A disulfide group is sensitive on a catalytic reaction. The result of this simple catalytic reaction is the cleavage of the *bis*-form into two separate molecules. This process is reversible. The cleaved molecule, called *mono*-form, has enough molecular characteristics to be another assembly building unit. Therefore, the disulfide group is an external force–specific functional segment for the *bis*-form. The thiol group becomes an external force–specific functional segment for the *mono*-form. The assignment of the rest of the segments is straightforward. The undecyl hydrocarbon chain is an attractive segment because of its capability of generating attractive hydrophobic force. And the trimethylammonium group is a repulsive segment. It induces an electrostatic repulsive force when the assembly takes place. This assignment is valid for both forms.

Figure 9-4(b) shows how the assembled systems of this building unit respond to a simple catalytic reaction. The *bis*-form, as with the *trans*-form in Figure 9-3, can be considered as a *bola*-form amphiphile. Two attractive segments directly interact with those from neighboring building units as if one long hydrocarbon chain brings them together. The repulsive segments at both ends counterbalance this attractive process. This forms a bilayer type of planar micelle. The *cmc* value should be much lower than that of the *mono*-form. If there is a higher-order assembly, there will be a strong chance for the *bis*-form to form a lamellar type of liquid crystal. Let us now induce the catalytic reaction with the *bis*-form. The attractive and repulsive forces are almost the same for both forms. For the *bis*-form, there are two attractive segments and two repulsive segments. For the *mono*-form, there is one of each segment. However, the number of building units for the *mono*-form is actually doubled from that of the *bis*-form. This means that the number densities of the attractive and repulsive segments are the same for both forms. It can be also stated that the ratio of the attractive segment to the repulsive segment is the same for both forms. The difference is in the external force–induced directional factor. It works *against* the molecular geometry when the catalytic reaction converts the *bis*-form into the *mono*-form. As the external force–induced directional factor goes into action, the *mono*-form that is less assembly favorable begins to appear, which gradually makes the whole assembly less favorable compared with the *bis*-form only. At the end, the assembly system with the *mono*-form only forms aggregates whose morphology becomes close to a spherical-like globular micelle. The *cmc* value should be higher than that of the *bis*-form. The higher-order assembly would

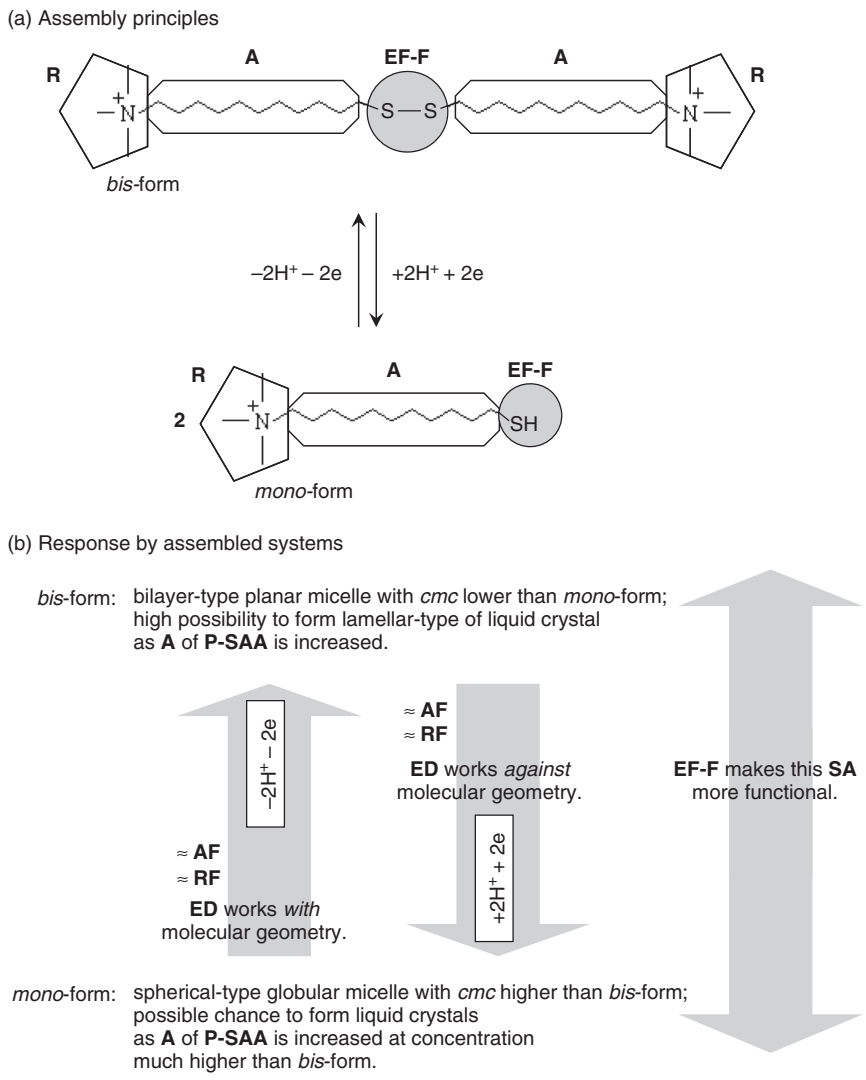

Figure 9-4. Catalytic reaction–responsive molecular self-assembly. **A, R**, and **EF-F** refer to attractive, repulsive, and external force–specific functional segments, respectively. **AF** and **RF** refer to attractive and repulsive forces, respectively. **ED** is external force–induced directional factor. **SA** and **P-SAA** are short for self-assembly and primary self-assembled aggregate, respectively. *cmc* is critical micellar concentration.

form a liquid crystal structure. But the concentration where the initial liquid crystal appears should be much higher than that of the *bis*-form. When the catalytic reaction changes the *mono*-form back into the *bis*-form, the external force–induced directional factor now works *with* the change in the molecular geometry. It means that it works in the same direction of the packing when the configuration changes.

This makes the assembly more favorable. As long as the chemical integrity of both forms of the building units is tolerant enough to repeat the catalytic reaction, this functional assembly continues reversibly.

9.3.1.3. Electrochemical-Responsive Assemblies. The building units in Figure 9-5 are sensitive on an electrochemical reaction. The condition is also in water at room temperature.

Figure 9-5(a) shows their molecular structures. A key point is at the ferrocenyl group that is attached at the end of the long hydrocarbon chain (the one on the left-hand side). By using a proper condition for an electrochemical reaction (electrochemical oxidation/reduction), this group (as a group, not in terms of the charge of iron atom) can be converted from a neutral form (ferrocenyl group) into a positively charged form (ferroceniumyl group), and vice versa (Gallardo and Abbott, 1997; Gallardo et al., 1996). This conversion makes fundamental changes in their assembly. It thus is inevitable that this ferrocenyl group should be assigned as its external force–specific functional segment. When the electrochemical reaction causes this group to be positively charged, it will induce a significant repulsion during the assembly. If the condition, on the other hand, is to have this group be neutral, it will still have some degree of repulsion due to its bulkiness. But it will be much less significant than the electrostatic repulsion from the charged group. For both forms, the other end of the building units has a trimethylammonium group. This is one of the most common repulsive segments. Also, for both forms, the pentadecyl hydrocarbon chain becomes their attractive segment. This chain is long enough to generate an attractive hydrophobic force between them. This segmental analysis now says that, for the form on the left-hand side, it almost looks like a typical cationic amphiphile with a bulky neutral group at the one end. The *mono*-form is named for this because of this structural resemblance. For the one on the right-hand side, its assigned name, *bola*-form, comes from its structural resemblance to a *bola*-form amphiphile.

The *bola*-form amphiphiles have two head groups at both ends of their long hydrocarbon chains. When the two head groups are the same, they are called homo-type *bola*-amphiphiles whereas the hetero-type is for *bola*-amphiphiles with two different head groups. For this *bola*-form of building unit, the ferroceniumyl group becomes its second repulsive segment. Lastly, both the ferrocenyl and ferroceniumyl groups might have some degree of directional force capability due to their geometrical features. They could induce a side-by-side type of molecular packing. However, it is highly likely that the strong attractive force from the long hydrocarbon chain and its counterbalancing by the strong electrostatic force cause the ferrocenyl or ferroceniumyl group to be arranged in a random manner. Therefore, it is reasonable to assume that a directional interaction from the ferrocenyl and ferroceniumyl groups becomes negligible.

Figure 9-5(b) shows how the assembled systems of the building unit respond to an electrochemical signal. When the *bola*-form of building unit self-assembles, the attractive force from the long hydrocarbon chain is strong enough to bring them together at the initial stage of the process. However, since there are two repulsive

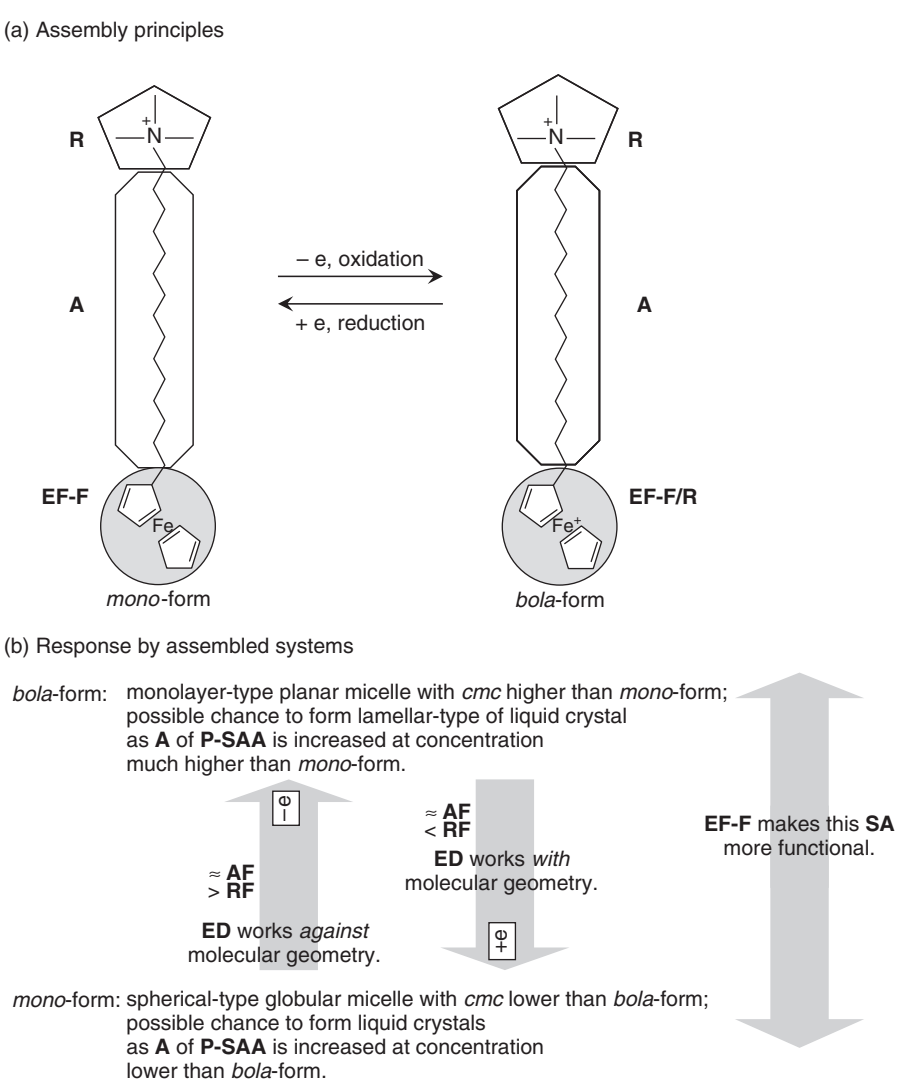

Figure 9-5. Electrochemical-responsive molecular self-assembly. **A, R**, and **EF-F** refer to attractive, repulsive, and external force–specific functional segments, respectively. **AF** and **RF** refer to attractive and repulsive forces, respectively. **ED** is external force–induced directional factor. **SA** and **P-SAA** are short for self-assembly and primary self-assembled aggregate, respectively. *cmc* is critical micellar concentration.

segments at both ends of this hydrocarbon chain, the repulsive force that counterbalances the attractive force becomes much stronger than that of the *mono*-form. This particular force balance combined with the geometric characteristic of the *bola*-form can make its aggregate a monolayer type. The *cmc* value should be much higher than that of the *mono*-form. The condition for higher-order assembly

cannot be easily achieved for this building unit because of this strong repulsive force. If, however, that actually happens to be the case, the most likely higher-order aggregate is liquid crystals with a lamellar type of morphology. And the concentration where the higher-order aggregate first appears will be much higher than that of the *mono*-form. Now let us consider the condition where the electrochemical signal converts the cationic ferroceniumyl group into a neutral one. The attractive force remains the same since there is no change in the attractive segment. The repulsive force, on the other hand, is reduced significantly. Simply stated, the electrostatic repulsive force induced by the ferroceniumyl group is no longer present. The external force–induced directional factor works *with* the molecular geometry of the building unit, which means that it works in the same direction of molecular packing when the molecular configuration is changed from the *bola*-form into the *mono*-form. This is one of the typical changes in segmental structures that should provide more favorability for the assembly system. The *mono*-form has a higher chance of forming the primary aggregates with a spherical-type of morphology. Its *cmc* value should be much lower than that of the *bola*-form. The possibility of higher-order assembly is higher than for the *bola*-form. It is likely that the higher-order aggregate will form a liquid crystal with three-dimensional symmetry such as cubic. Also, the concentration where the initial higher-order aggregates appear should be lower than that of the *bola*-form. When the electrochemical signal reverses the state of the ferrocenyl group, that is, to be charged, the segmental situation will be reversed as well. The repulsive force is increased because of the increased electrostatic repulsive force. The external force–induced directional factor now works *against* the molecular geometry while the attractive segment remains the same. This makes assembly less favorable.

The electrochemical-responsive self-assemblies and their self-assembled aggregates can find various applications in a diverse field of technologies, which is not limited to nanotechnology. Some details on nanotechnology systems will be introduced in later chapters. Overall, it is again the external force–specific functional segment that provides a unique functionality for this assembly system. For more details about the chemistry and interfacial properties of this particular molecule, please refer to Gallardo and Abbott (1997) and Gallardo et al. (1996).

9.3.1.4. Solution pH–Responsive Assemblies. Figure 9-6 shows solution pH–responsive molecular self-assemblies. Their building units have a segment that is sensitive on solution pH. The assemblies take place at room temperature (25 °C) in water.

The molecular structure of the building units and their assembly principles are shown in Figure 9-6(a). The one at the top is dodecyldimethylamine oxide in its nonionic form while the one at the bottom is its cationic form. The terms *nonionic*-form and *cationic*-form come from this. The variation between the two forms is determined by the changes in solution pH. For both forms, it is clear that the dodecyl hydrocarbon chain is their attractive segment. It induces a typical attractive hydrophobic force. The effect of the changes in the head groups (by the changes in solution pH) on the hydrophobic force is minimal. When the pH favors

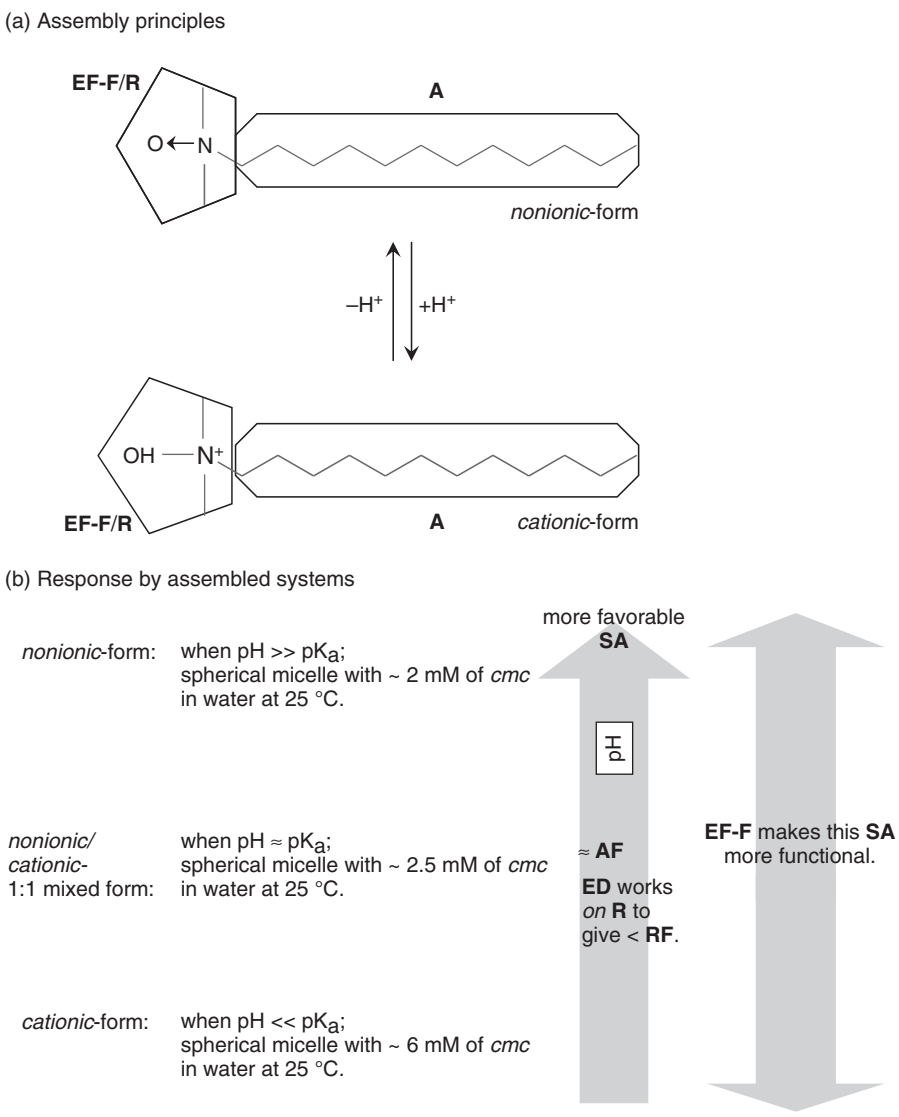

Figure 9-6. Solution pH–responsive molecular self-assembly (**SA**). **A, R**, and **EF-F** refer to attractive, repulsive, and external force–specific functional segments, respectively. **AF** and **RF** refer to attractive and repulsive forces, respectively. **ED** is external force–induced directional factor. *cmc* is critical micellar concentration.

the building unit being in a *nonionic*-form, its head group remains nonionic. This means that the head group can induce a repulsive hydration force. When the pH is varied so that the building unit becomes a *cationic*-form, in other words, when the head groups have the positively charged nitrogen atom, the head group can induce a repulsive electrostatic force. These are two extreme situations in reality.

However, for both cases, the head groups work as a repulsive segment, and at the same time, they are sensitive on the pH changes, which in turn change the degree of the repulsive force. Thus, the head groups become an external force–specific functional segment as well.

Figure 9-6(b) shows how the assembled systems of the building units respond to solution pH. When the pH is much smaller than the pK_a value, it is reasonable to assume that the building unit is almost solely present in the *cationic*-form. Then, its segmental structure becomes the same as a typical cationic surfactant. The dodecyl chain brings the building units together and the cationic head group counterbalances them. This is one of the most common segmental structures that form spherical micelles. At 25 °C in water, its *cmc* value is ~6 mM. Let us now assume that the pH is gradually increased so that it becomes close to the pK_a value. Dodecyldimethylamine oxide then comes close to a 1:1 mixed form of the *nonionic*/*cationic*-forms with a narrow range of variation. When compared with the pure *cationic*-form, the attractive segment should be the same. There simply is no reason why the hydrophobic attractive force induced by the hydrocarbon chain should be changed by the pH changes. The external force–induced directional factor, on the other hand, works *on* the repulsive segment, inducing a significantly reduced repulsive force. The number of cationic head groups that induce the electrostatic repulsive force is reduced, and the subsequently generated nonionic head groups not only induce the hydration force rather than the electrostatic force but screen the electrostatic force as well by locating in between the cationic head groups. The same attractive force with a reduced repulsive force is a typical situation that makes the assembly more favorable. The decreased *cmc* value of ~2.5 mM from the *cationic*-form at the same condition strongly backs up the validity of this analysis. Since there are no directional and asymmetric packing segments, the morphology of the micelle of this mixed form comes close to spherical.

Let us now assume that the pH is increased even further so that it is now much larger than the pK_a value. The dominant form of dodecyldimethylamine oxide is the *nonionic*-form. The attractive segment is not affected by this change. The external force–induced directional factor continues to work *on* the repulsive segment and provides a further reduction in its repulsive force. It may be reasonable to assume that the cationic head groups are no longer present or that their amount is negligible. There is no more electrostatic repulsive force, and the counterbalancing against the attractive hydrophobic force comes from the repulsive hydration force whose operating range and strength are less than the electrostatic force. Once again, the same attractive force with a reduced repulsive force makes the assembly more favorable. The *cmc* value of the *nonionic*-form at the same condition is indeed further decreased to ~2 mM.

Case Study 9.1

Self-assembly of pyrene-β-cyclodextrin dimer that is responsive on host–guest complexation (Ogoshi et al., 2010) offers a good example for the external signal–responsive molecular assembly. This rather complicated molecular dimer

has all five assembly segments. The van der Waals force and π–π stacking interaction are its attractive segment while steric repulsion is its repulsive segment. It has a number of hydrogen bonding groups on the cyclodextrin groups, which are the directional segment. A number of asymmetric centers, which are also on the cyclodextrin groups, are its asymmetric packing segment. Its asymmetric molecular geometry also contributes to this segment. The two cyclodextrin groups are those having the host–guest complexation capability, thus they are the external force–specific functional segment of this dimer. Without any additives, this dimer in aqueous solution self-assembles into helical nanowire. This comes as no surprise since the attractive and repulsive segments are well balanced. The directional segments are abundant and strong enough to direct the whole assembly into a long-wire type of morphology. The morphological chirality is induced by the asymmetric packing. Once the guest molecule (sodium adamantane carboxylate) is introduced into this self-assembled aggregate, the helical nanowire is transformed into a J-type of aggregate. Sodium adamantane carboxylate is complexed with the cyclodextrin groups. The authors' results show that this complexation weakens the π–π stacking of the phenylethynylpyrene segments while it promotes the electrostatic repulsive force and steric hindrance between the complexed anions. In terms of segmental analysis, this means that the attractive force is reduced while the repulsive force is increased. The directional and asymmetric packing segments are intact during the complexation. This change makes the assembly capability a little less favorable. The directional assembly and asymmetric packing should be still in full action. Therefore, the most reasonable prediction for the self-assembled aggregate is the change of the helical nanowire into a less compact but still linear form, which is characteristic of J-type aggregate.

9.3.2. External Signal–Responsive Colloidal Assemblies

Figure 9-7 shows the schematic explanation of the effect of external signals on nanoassembly systems consisting of external signal–responsive colloidal building units. The symbols for each segment are the same as for molecular building units in Subsection 9.3.1.

First, let us assume that there is a spherical colloidal particle with an attractive segment and a repulsive segment, and they are well balanced at the condition given here. This, in other words, means that they have a clear self-assembly capability. Now let us assume that there is another segment within the particle and this segment is sensitive on external signals. For many colloidal particles, this external force–specific functional segment is the colloidal particle itself. Its intrinsic property as a whole or a specific group that is a part of the particle is usually the part that senses external signals. Paramagnetic or ferromagnetic nanoparticles are good examples. They can have their own attractive and repulsive segments, and their magnetic property becomes an external force–specific functional segment. This is why the symbol representing an external force–specific functional segment is not included in this figure. If the functional segment yields more attractive interaction

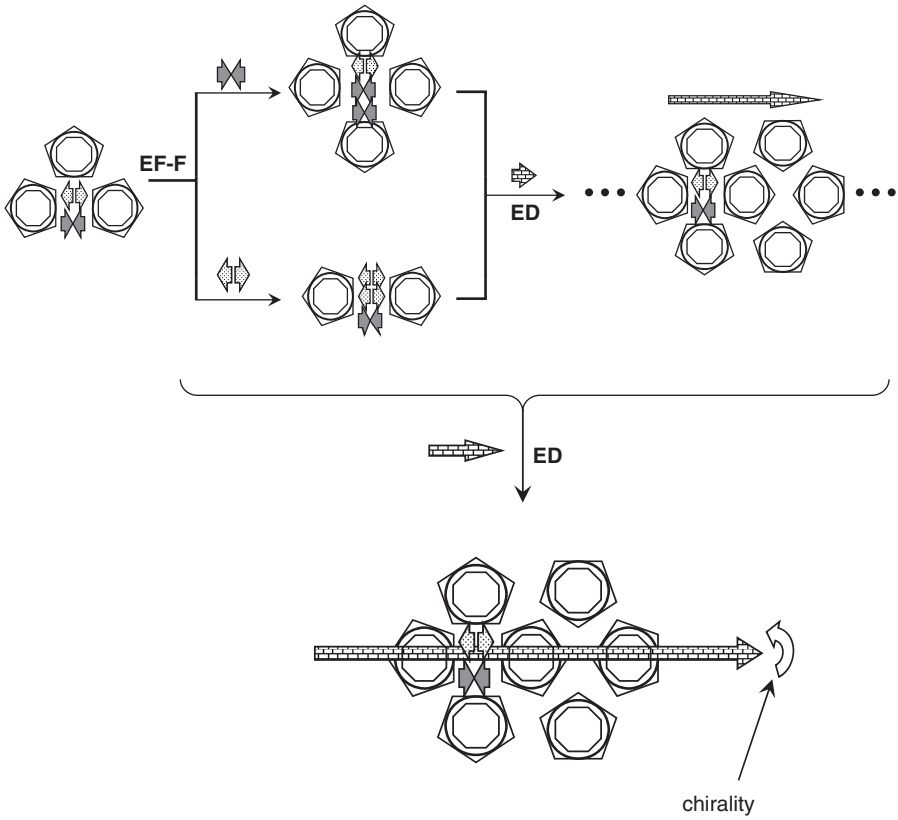

Figure 9-7. Schematic explanation of the nanoassembly with external signal–responsive colloidal building units. **EF-F** refers to external force–specific functional segment. **ED** is external force–induced directional factor.

during the assembly, it will provide more favorability for the system. If it yields more repulsive interaction, it will provide less favorability.

Let us suppose that an external signal of interest is imposed on the solution that contains the colloidal particles. Common external signals are magnetic field, electric field, and flow. These all generate an external force–induced directional factor that works to direct the assembly. For self-assembled aggregates, this directional effect makes their morphologies asymmetric. The directional segment of the colloidal particle is not included in the scheme. If it has one, its impact on the aggregates is determined by its vectorial sum with the external force–induced directional factor. If the two work cooperatively, the degree of asymmetric nature will be increased. If they work against each other, it will be decreased. If it happens to be the case that the two directional forces completely compensate each other, the apparent result induced by them would be minimal or vanish from the aggregates. As for the molecular assembly systems in Figure 9-2, external signals often induce asymmetric packing. This external force–induced asymmetric

packing can happen at any stage of the colloidal assembly. It can be induced whether the functional segment promotes more favorable or less favorable assembly. It can also be induced whether the external force–induced directional factor makes the assembly more directional or less directional.

9.3.2.1. Thermo-Responsive Assemblies. Figure 9-8 presents a thermo-responsive colloidal self-assembly. Its building unit is a polymeric colloidal particle that is sensitive on changes in temperature.

Figure 9-8(a) shows a microgel (or hydrogel) particle of poly(*N*-isopropylacrylamide). Like most of the polymeric particles, these microgel particles also have an attractive interaction between them through van der Waals force. This therefore is its attractive segment. With the assumption that the surface of this colloidal particle is stabilized with a part of the polymer chains outwardly protruding, the steric repulsive force that is induced by this chain becomes its repulsive segment. The amide group is embedded inside the particle with possibility of local heterogeneity. And this is the group whose physical property is sensitive on changes in temperature, which can affect the size and morphology of the particle. Hence, this amide group should be assigned as its external force–specific functional segment. Furthermore, this segment is located anywhere

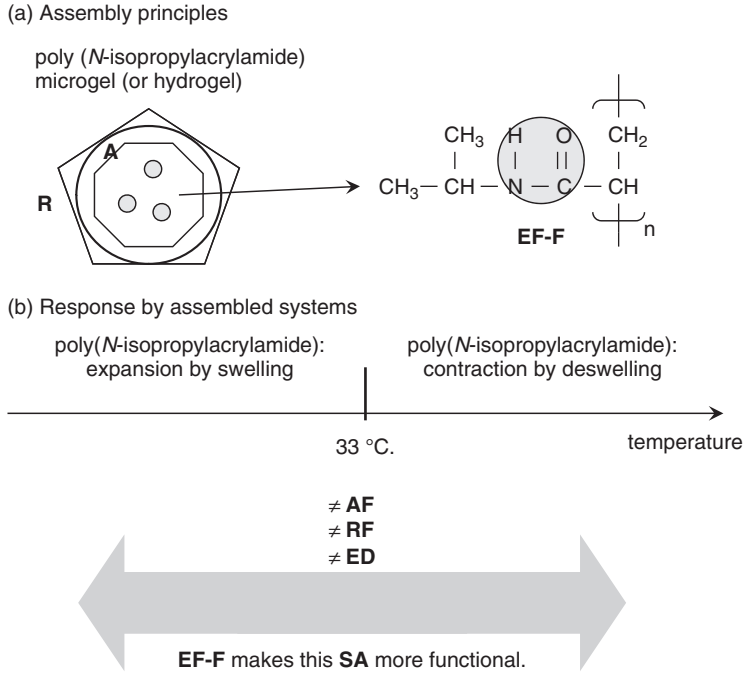

Figure 9-8. Thermo-responsive colloidal self-assembly (**SA**). **A, R**, and **EF-F** refer to attractive, repulsive, and external force–specific functional segments, respectively. **AF** and **RF** refer to attractive and repulsive forces, respectively. **ED** is external force–induced directional factor.

within the particle. For molecular building units, the external force–specific functional segments have a specific location within the molecules. This makes one key difference between the colloidal and molecular building units when they are under external signal during assembly.

Figure 9-8(b) shows how the assembled systems of poly(*N*-isopropylacrylamide) particles respond to temperature changes. At the critical temperature of 33 °C (which is commonly known as *lower critical solution* temperature), the particle experiences a dramatic physical change. Below this temperature, it swells due to the hydration, which is mainly induced by the amide group. As the degree of this swelling is increased, the inside of the particle builds up an increased outward pressure, which results in an expansion of the particle. Above the critical temperature, it deswells due to the dehydration, which is also mainly induced by the amide group. The result is a contraction of the particle. This expansion–contraction makes precise tracking of the segmental structures difficult. It is not only the size of the particle that is changing, but its composition, and the density of the surface chains is changing as well. A reasonable analysis for this situation is not to attempt to predict the degree of changes in each segment, but to see whether there is any significant variation. For this particular colloidal particle, it will be safe to assume that both the attractive and repulsive segments experience significant changes below and above the critical temperature. The external force–induced directional factor might not be that significant, but if there is any, it will also change at this temperature. Especially when colloidal particles have nonspherical shapes such as tube or rod, or derived shapes such as hollow sphere or core-shell, both the direction and magnitude of the external force–induced directional factor will be markedly changed by the temperature change. A silica colloidal particle whose surface is coated with this poly(*N*-isopropylacrylamide) shell is a good example of a core-shell type.

In terms of the assembly of the colloidal particles, both below and above 33 °C, they self-assemble under an assumption that the balance between the attractive and repulsive forces favors it. But since the size and composition of the particles are different, it can be expected that the outcome of the assembly will not be the same. It is likely that the aggregates above this temperature would have more symmetric morphology with less fractal-like defects. Moreover, the assembly and morphology of the aggregates will experience dramatic changes whenever this assembly system is going through this critical temperature. A review presented by Saunders and Vincent (1999) provides details on the syntheses and properties of this particular microgel. It also describes the molecular mechanisms for its swelling and deswelling processes. Only intermolecular interactions are involved in the molecular mechanisms, and it will be intuitive to track them with the bases of the force balance concept presented here.

9.3.2.2. Solution pH–Responsive Assemblies. Figure 9-9 presents a colloidal self-assembly system that is responsive on solution pH. Figure 9-9(a) gives its assembly principles. The colloidal building unit is poly(acrylic acid) microgel (or hydrogel). With the same logic as for the poly(*N*-isopropylacrylamide) particle

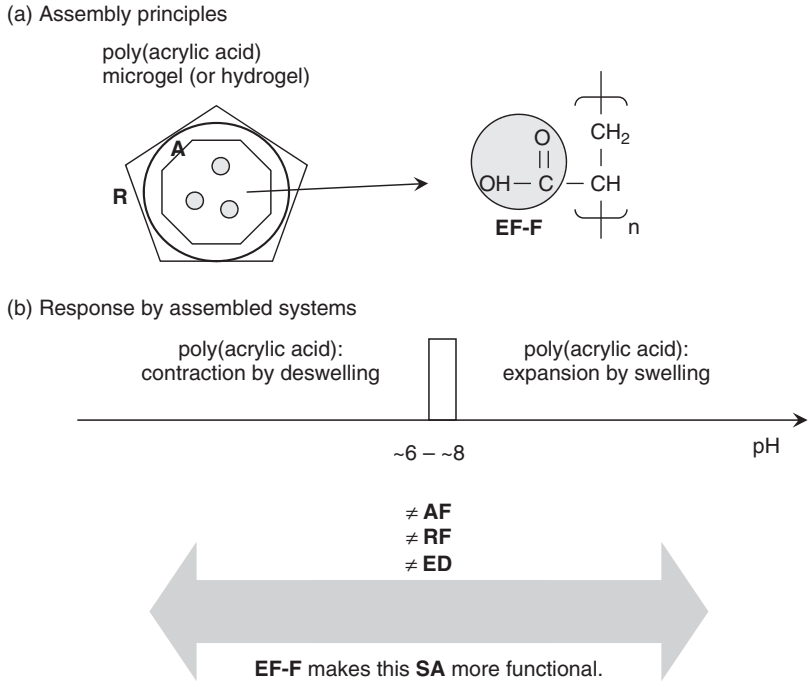

Figure 9-9. Solution pH–responsive colloidal self-assembly (**SA**). **A, R**, and **EF-F** refer to attractive, repulsive, and external force–specific functional segments, respectively. **AF** and **RF** refer to attractive and repulsive forces, respectively. **ED** is external force–induced directional factor.

in the previous subsection, it can be stated that this particle has both attractive and repulsive segments. Poly(acrylic acid) has carboxylic group side chains along its backbone, which is sensitive on the pH change (protonation and deprotonation). This sensitivity on the pH is responsible for the changes in physical properties of the particle. It thus is this carboxylic group that becomes its external force–specific functional segment. It is not easy to pinpoint the specific location of this functional group. It would be a fair assumption that this segment is evenly distributed within the particle.

Figure 9-9(b) shows how the assembled systems of this building unit respond to the pH. The pH-responsive functional segment triggers a dramatic change in the particle sizes at a pH of ~6–~8. As pH is decreased below this range, the particle deswells by the act of the carboxylic group, which results in the contraction of the whole particle. As pH is increased above this range, it swells, which results in the expansion of the whole particle. This is a reversible process. In addition, it is not only the particle sizes that vary, but the composition and possibly the density of the surface charge as well. This may make the changes in the attractive and repulsive segments difficult to analyze. However, it is certain that both segments experience significant changes during the pH change. As in the previous example, the external

force–induced directional factor might not be very significant for this system. If there is any, it will also be noticeably different below and above this range of pH. And it will be more prominent when the particle is nonspherical. The attractive and repulsive segments favor assembly despite the pH changes. There is a slight possibility, as far as the segmental structure is concerned, that the assembly will be disrupted when the system goes through the critical pH range. However, since the segmental structure below and above this pH range is markedly different, it would be safe to state that the assembly and its outcome will be very different. As in the previous subsection, the aggregates formed below the critical pH range will show more symmetric morphology with fewer defects. For the syntheses and properties of diverse pH-responsive microgel particles, please refer to Tan and Tam (2008). Molecular mechanisms for their swelling and deswelling processes are also given, which can be understood based on the force balance among the intermolecular interactions involved.

9.3.2.3. Magnetic Field–Responsive Assemblies. Figure 9-10 shows a colloidal self-assembly system that is responsive on external magnetic field. For this system, the colloidal particle is assumed to be rod-shaped.

Figure 9-10(a) has an iron oxide colloidal rod. Let us assume that its size is in the nanometer scale. And iron oxide is one of the most typical ferromagnetic materials.

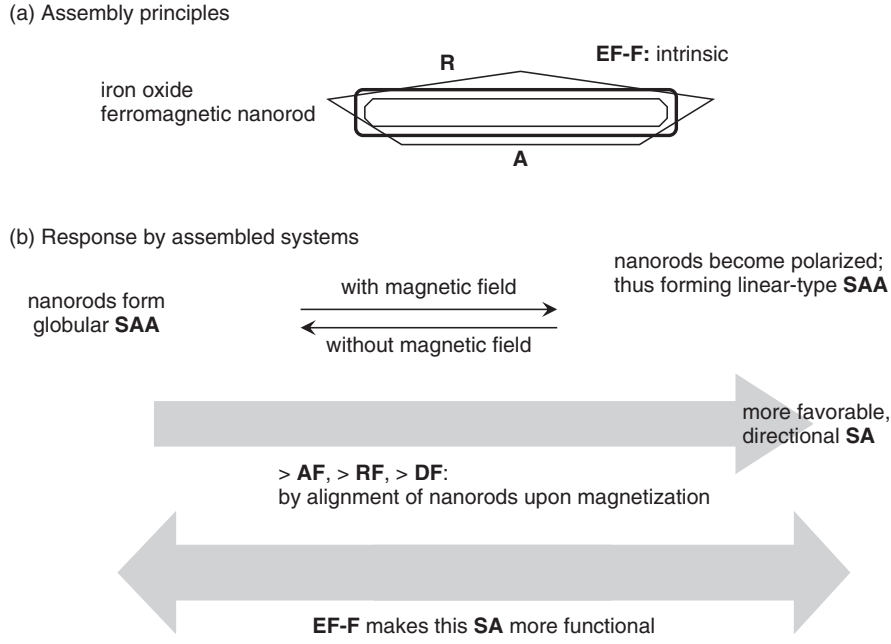

Figure 9-10. Magnetic field–responsive colloidal self-assembly. **A, R**, and **EF-F** refer to attractive, repulsive, and external force–specific functional segments, respectively. **AF, RF**, and **DF** refer to attractive, repulsive, and directional forces, respectively. **SA** and **SAA** are short for self-assembly and self-assembled aggregate, respectively.

The term *ferromagnetic nanorod* comes from this. The nanorod is represented as a bold-lined rectangle in the figure. It also shows the segmental structure. The rod-shaped long octagon indicates the attractive segment while the deformed pentagon is for the repulsive segment. It is also assumed that there is no modification on the surface of the nanorod. Thus, the attractive force comes from van der Waals interaction. The repulsive force, on the other hand, is assumed to come from the surface charges. The external force–specific functional segment is the ferromagnetic property that varies when the nanorod is placed under magnetic field. Hence, this functional segment is the nanorod itself.

Figure 9-10(b) shows the effect of magnetic field. When there is no magnetic field, the assembly would still take place. The force balance between the attractive and repulsive segments is there. An important difference from the previous two subsections is that at this time it has a stronger tendency to be asymmetric rather than symmetric. For the nanorod, its rodlike shape itself becomes the origin of another colloidal force during assembly. It is a capillary force acting between them. It runs through the long-axis of the nanorod, thereby becoming a directional force. In addition, since the strength of this force is comparable to that of the attractive and repulsive forces, it can make a significant difference on the whole force balance. Obviously, the result will be more asymmetric morphology of the aggregates. Now let us consider the situation that a proper strength of magnetic field is imposed on this system. The nanorods first will be polarized by the magnetic field. It then will provide a directional magnetic attraction between them. An attractive force is increased as the strength of the magnetic field is increased. The surface charge is not affected by the magnetic field. But the repulsive force between the nanorods is also increased as they become polarized. Thus, the overall repulsive force is increased under magnetic field. The magnetic attractive interaction between the polarized nanorods works along the direction of their two poles, which means that this alignment of nanorods by the magnetization actually promotes the directional force between them. Both the attractive and repulsive forces are increased, but nearly to the same degree. And the directional force is increased substantially as well. This implies that the assembly should become more favorable and directional. The assembly takes place at a lower number concentration of nanorods under magnetic field, and the morphology of their aggregate becomes asymmetric and linear.

This particular system was to show the general scheme for asymmetric colloidal assemblies. There are many other examples that fit into this. A poly(pyrrole)-based polymeric nanorod is another good example. Since poly(pyrrole)-based polymer is a typical conducting polymer, its assembly becomes responsive on external electric field. Both magnetic field– and electric field–responsive colloidal assembly systems have great implications for a diverse range of nanotechnology systems.

Case Study 9.2

A detailed theoretical study on the self-assembly of semiconducting nanorods shows the importance of balancing all the forces involved during the assembly process (Titov and Král, 2008). van der Waals and Coulomb interactions on this

modeling can be viewed as the attractive and repulsive segments, respectively. The authors also investigated the effect of external electric field. The intrinsic property of the nanorods that is responsive on electric field is the external force–specific functional segment. Their study also recognizes the importance of the relative strength of external signal to the force balance between the attractive and repulsive segments for the control of the assembly direction. The work regarding the self-assembly of cadmium selenide nanorods under external electric field reinforces this notion experimentally (Gupta et al., 2006).

Case Study 9.3

The study on the controlled self-assembly of nanoparticles and microparticles at a two-fluid interface under electric field is also very instructive (Aubry and Singh, 2008). It deals with spherical particles, not asymmetric ones. But it expands the concept of force balance into interfacial colloidal self-assembly. The effect of the strength of the electric field on the balance between the attractive capillary and repulsive electrostatic forces (both magnitude and direction) is well demonstrated. This control of the force balance makes it possible to manipulate the equilibrium distance between the particles; thus it assembles a virtually defect-free monolayer. This article also studies the buoyancy effect. It shows that the vertical force balance of buoyant weight balanced by vertical capillary and electrostatic forces determines the vertical position of the particles. The attractive capillary and repulsive electrostatic forces are the attractive and repulsive segments, respectively. As in the previous case study, the intrinsic property of the particles, which is assumed to be perfectly dielectric so that they become responsive on the electric field, is the external force–specific functional segment for this assembly system. In addition to that, this system has an external force–induced directional factor that is promoted by the interface. This factor provides the directionality to the assembly system, thus making the assembled system a monolayer.

Case Study 9.4

The study that was interpreted based on segmental analysis in Chapter 3 (Case Study 3.4) (Butter et al., 2003) describes the effect of external magnetic field on the self-assembly of superparamagnetic iron nanoparticles as well. Their nanoparticle is also spherical, and it clearly shows the impact of the additional attractive segment and the external force–induced directional factor on the assembly. The superparamagnetic property of the iron nanoparticle is its external force–specific functional segment. Case Study 3.4 provides a detailed interpretation of each segment and their force balance during assembly.

Case Study 9.5

Case Study 4.3 in Chapter 4 showed the colloidal self-assembly system whose aggregates are formed through the balance between the attractive critical Casimir

force and the screened repulsive Coulomb force (Bonn et al., 2009). What is more for this system is a temperature-dependent aggregation because of the temperature-dependence of the Casimir force. Above the aggregation temperature, the critical Casimir force induces particle assembly, while, below it, the repulsive force disassembles the aggregates into homogeneous suspension. Thus, temperature, which is the external signal here, provides an effective tool to manipulate the force balance between the particles, thereby controlling their assembly.

9.4. COLLECTION OF EXTERNAL SIGNAL–RESPONSIVE ASSEMBLY SYSTEMS

Table 9-1 lists the assembly systems whose assemblies are responsive on external signals. As shown, the types of building units that are responsive on external signals are surprisingly diverse. They can be molecular, polymeric, colloidal, bio-mimetic, and biological. Some of them have quite simple structures. But, for many, to be external-signal responsive, they have to have a part that is responsive on external signals. This usually makes their structures a little more complicated and specific than ordinary building units. For most of these specific building units, references are given at the end of the table. These should help clarify more details about each building unit and their assemblies. The external signals that are comparable with the building units are also diverse. Many external signals, such as electric field, magnetic field, flow, and ultrasound, are imposed purely from outside each assembly system. But for many others, such as host–guest complexation, charge transfer, gas adsorption, and metal complexation, the signals actually come from inside each assembly system. The response by assembled systems to each external signal is also shown in the table. This response includes not only the morphological changes of assembled systems, but their changes in configurations and intermolecular conversions as well. These diversities in external signal–responsive assembly systems in turn make the development of external signal–responsive nanomaterials more practical.

9.5. FROM ASSEMBLY SYSTEMS TO NANOMATERIALS

One of the key issues in practice for the assembly of external signal–responsive nanomaterials is how to get the individual assembly system into nanomaterials whose functionalities properly reflect the characteristics of the assembly system, in other words, how to assemble the assembly systems without having them lose their capability to respond to external signals.

There are four common situations where most of the functional nanomaterials should function: as bulk nanomaterials, as nanomaterials in solution, as assembled systems inside nano- or macro-pores or interstitial regions in between solid layers, and as assembled systems on surfaces. For the first two situations, a simple scale-up

TABLE 9-1. Collection of external signal–responsive nanoassembly systems.

Building Unit	External Signal	Response by Assembled System
4,4′-bis[{n-(trimethylammonio) alkyl}]oxy]azobenzene	light	bilayer-type micelle ↔ globular micelle
n,n′-dithiobis [alkyltrimethylammonium]	catalytic reaction	bilayer-type micelle ↔ globular micelle
n-ferrocenyl-N,N,N-trimethyl alkanaminium bromide	electrochemical	monolayer-type micelle ↔ globular micelle
alkyldimethylamine oxide	pH	spherical micelles with different surface charge
poly(*N*-isopropylacrylamide) hydrogel	temperature	expansion ↔ contraction
poly(acrylic acid) hydrogel	pH	expansion ↔ contraction
ferromagnetic nanorod	magnetic field	linear aggregate ↔ globular aggregate
superparamagnetic nanorod	magnetic field	linear aggregate ↔ globular aggregate
semiconductor nanorod	electric field	linear aggregate ↔ globular aggregate
phenylethynylpyrene-β-cyclodextrin dimer[1]	host–guest complexation	helical (chiral wire) ↔ J-aggregate
latex nanoparticle in refractive index-matched solvent[2]	temperature	assembly ↔ disassembly
stilbene amide-α-cyclodextrin[3]	light	dimer ↔ pentadecameric aggregate
surfactants, amphiphiles	flow	homogenous micelles ↔ elongated/aligned micelles
nanoparticles, colloids	ultrasound	disassembly ↔ reassembly
azobenzene-based cationic surfactant[4]	light and host–guest complexation	assembly ↔ disassembly of vesicle
polyimide-based polymer having hexaoxyethylene chain[5]	charge transfer	stacked folding ↔ unfolding (intra-self-assembly)
cholic acid–based cationic amphiphile[6]	pH	~20-fold *cmc* change and hierarchy
cholic acid–based tetraaminocalixarene[7]	solvent	micelle-like ↔ reverse micelle-like
poly(phenylacetylene) having cyclodextrin groups[8]	host–guest complexation	helicity inversion
T-shaped amphiphilic dendrimer[9]	ultrasound/solvent	dodecameric micelle ↔ heptameric micelle
cholic acid–based steroid cyclophane[10]	surface pressure	piezoluminescence via dynamic molecular recognition
alkyl (dodecyl, hexadecyl) amidine[11]	gas (carbon dioxide)	emulsion stabilizing/breaking, switchable demulsifier
oligoheterocyclic strand with pyridine/pyrimidine units[12]	metal ion/pH	helical coil ↔ linear chain

(*continued*)

TABLE 9-1. (*Continued*)

Building Unit	External Signal	Response by Assembled System
silica colloidal particle[13]	ac electric field	hard disk fluid ↔ dipolar chain ↔ hcp crystal
phenylacetylene oligomer[14]	solvent/temperature	helical coil ↔ open chain
proteins[15]	electron transfer	folding ↔ unfolding
naphthyridinyl urea derivatives[16]	concentration	intramolecular folding ↔ intermolecular dimerization
oxybispyridine-based complexes[17]	counteranion exchange	contraction ↔ expansion of helical pitch
β-cyclodextrin-based organogel[18]	temperature	assembly ↔ disassembly
schizophrenic block copolymer[19]	temperature, pH, ionic strength	micellar inversion; normal micelle ↔ inversed micelle

Most of the building units that are shown in Table 1-13.

[1] Ogoshi et al., 2010. For more about the external signal–responsive self-assembly of the building units containing chromophores, or of π-conjugated molecules and polymers, please see the references therein.
[2] Bonn et al., 2009.
[3] Yamauchi et al., 2008.
[4] Wang et al., 2007.
[5] Ghosh and Ramakrishnan, 2005.
[6] Zhong et al., 2005.
[7] Ryu and Zhao, 2004.
[8] Maeda et al., 2006. Please see the comprehensive references therein for more examples for external signal–responsive helicity inversion.
[9] Jäger et al., 2010.
[10] Ariga et al., 2005.
[11] Liu et al., 2006.
[12] Barboiu and Lehn, 2002.
[13] Juárez and Bevan, 2009. See their quantitative calculation for the balance among all the forces involved for this colloidal self-assembly.
[14] Nelson et al., 1997.
[15] Telford et al., 1998.
[16] Corbin and Zimmerman, 2000.
[17] Jung et al., 2000.
[18] Li et al., 2010.
[19] Buetuen et al., 2006.

of selected assembly systems is usually enough to achieve the desired functionalities. This is especially the case for nanomaterials in solution. However, for the bulk nanomaterials, it is often necessary to balance the assembly conditions with the conditions for the functions of the nanomaterials. For example, assuming that the purpose of a certain assembly is to have colloidal crystals that can change their functions by responding to temperature or pH, the assembly of selected colloidal system can be quite straightforward (details in Subsections 7.3.2 and 8.3.2), but to ensure their proper functionalities, it is necessary to have them in conditions where there is water or enough humidity. For the next two situations, the most often encountered issue is how to anchor the assembly systems on the surfaces of interest. Often, physisorption of assembly building units on the surfaces provides a strong enough force to ensure this. When this is the case, there is no need for an additional design of building units. However, it usually takes chemisorption or an even stronger interaction between the building units and the surfaces to have satisfactory stability and functionality of the nanomaterials. The most widely accepted solution for this situation is the concept of self-assembled monolayers (some specific examples are in Subsections 12.3.4 and 12.3.6), which can ensure both proper assembly and practicality. More details on this issue will be presented in the next few chapters whenever necessary.

External signal–responsive nanomaterials are often called *smart materials*. Yoshida and Lahann (2008) review some important aspects of them and two possible lines of approach to their design. Many smart materials work through the conformational transition of molecules under a stimulus. This article shows that the orientational transition of anisotropic colloidal particles can achieve the same functions. Lu and Liu (2007) review the stimuli-responsive assembly and disassembly of nanomaterials by using functional DNAs. These nanomaterials can respond not only to a single stimulus but to multiple chemical and biological stimuli as well. They also discuss the introduction of proofreading and error-correction mechanisms into nanomaterials assembly. (*Note:* The term *directed assembly* in this article corresponds to the term *directional assembly* used in this book.) Mendes (2008) reviews a number of surfaces that have switchable properties, "smart surfaces," based on self-assembled monolayers and polymer films. A variety of stimuli, including chemical/biological, thermal, electric field, and optical, have proved effective in controlling the properties of these surfaces both reversibly and irreversibly.

9.6. COLLECTION OF EXTERNAL SIGNAL–RESPONSIVE NANOMATERIALS

Table 9-2 lists the collection of external signal–responsive nanomaterials. This is not a complete collection. Rather, these are the most representative nanomaterials that frequently appear in the literature. Considering the research activity in this field and the diversity of the assembly systems that are responsive on external signals, many more will be forthcoming. The applications shown in the table are

TABLE 9-2. Collection of external signal–responsive nanomaterials.

External Signal–Responsive Nanomaterial	Application
light-responsive coating for functional glasses	sun glasses, energy-saving windows
electrochemical controlled optical materials	display panels
thermo-responsive nanogels and nanomaterials	medical devices
solution pH–responsive nanogels and nanomaterials	medical devices
drug- and gene-delivery systems: nanoparticles, micelles, emulsions, and liposomes (modified with functional groups)	medical devices
photorheological fluids	printing, inkjet, sensors
magnetorheological fluids	printing, inkjet, sensors
self-healing nanomaterials	construction materials, medical materials
crack and fracture resistance nanocomposite materials	construction materials, medical materials
temperature- and humidity-responsive nanoporous fabrics	clothes, energy-saving coating
temperature- and light-responsive nanocomposites (usually polymer with nanoparticles)	energy conversion devices, functional wall painting, high strength materials
functional films: changes into hydrophobic or hydrophilic surface by external signals	sensors
pH-responsive self-assembled monolayers	sensors
pressure-responsive films	energy-saving coating for vehicles

also the most representative ones for each nanomaterial. They certainly are not limited only to these. Not shown in the table is a key assembly principle for each nanomaterial. But the name itself strongly indicates what type of assembly system is needed to properly express the desired functionality. The selection of a specific assembly system is truly dependent on the specific purpose of each nanomaterial.

9.7. SUMMARY

Nanomaterials that have the capability to change their structures and properties by responding to physical/chemical signals have a broad scope of impact on nanotechnology. A key to the effective assembly of these functional materials is the building units whose assemblies are responsive on external signals. This chapter discussed the basics of the assembly principles and their relation to the assembly of functional materials. It showed that:

1. A careful structural analysis of the building units (segmental analysis) is useful to understand how the external signals affect their assembly processes and assembled systems.
2. A key part of the building units is the part whose structures or properties are responsive on external signals (external signal–specific functional segment).
3. This approach makes it possible for us to track external signal–responsive assemblies with a reasonable accuracy.

4. This in turn provides a good guide for the assembly design of external signal–responsive nanomaterials.

Finally, within the effective range of external signals, assembly systems usually respond to the signals in a gradual manner. But it sometimes can be chaotic. Also, assembly systems that can be responsive on multiple numbers of external signals may become critical for the assembly of certain nanotechnology systems.

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10

Nanomaterials with Intrinsic Functionalities

10.1. NANOISSUE

Some groups of nanoassembly systems can provide diverse physical or chemical functionalities when they are properly designed and assembled. The functionalities they show are intrinsic—in other words, these functionalities are delivered by the characteristics that are already embedded in their building units. The nanoassembly systems from Chapter 9 became functional by responding to signals provided from outside the building units. The term *intrinsic functionality* here emphasizes this difference within nanoassembly systems (for details on nanoassembly, see Section 2.1). Some typical intrinsic functionalities include the enhancement of reaction rate, catalysis, bio-comparability, and environmental susceptibility. In regard to nanomaterials, this difference implies that the functionalities of the external signal–responsive nanomaterials are mainly assembly processe–dependent while those with intrinsic functionalities are dependent mainly on the assembled systems. These two main types of nanomaterials often overlap when it comes to actual applications. However, the design of the assembly building units, assembly principles, and the working mechanisms of the functionalities are usually different, which makes it worth describing them in two separate chapters. Thus, the main issue in this chapter is:

Can we design an assembled system that shows a specific functionality?

If so,

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What are the key assembly principles?

and

How can it be assembled into nanomaterials?

The discussion begins with how to design each assembly segment (*segmental analysis*: see Subsection 1.2.2 for details), such as an attractive segment (for example, the hydrophobic part), a repulsive segment (for example, the hydrophilic part), and a functional/directional segment(s) (whenever these are necessary), and then how to rationally combine them to come up with an assembly system that can carry a specific functionality. The fields of bioinformatics and drug discovery already have shown the practicality of this approach, which is proven effective for the design of purpose-oriented drug molecules (Oprea and Blaney, 2006; "Piece by Piece," 2008; Rees et al., 2004; Vennila, 2006; Wyss and Eaton, 2007).

10.2. GENERAL OVERVIEW

Figure 10-1 shows a general overview of the design of nanoassembly systems whose assembled systems can show intrinsic functionalities. The first step is to identify how the assembly takes place, what its assembled system looks like, and how it functions under a given condition. This means identifying the nature of the nanoassembled system to be developed (for details on nanoassembled systems, see Section 2.6). The next step is to explore the options for each assembly segment. This almost always begins with an attractive segment. The reason for this is that, with only a few exceptions, an assembly cannot take place without the force that brings the building units together. An attractive segment generates an attractive force between the building units at the very first stage of the assembly. Table 1-1 presented a list of typical attractive segments with both the intrinsic components and the physical/chemical/conditional factors. Attractive segments are not limited to those in the table. A chemical space is vast (more on this aspect will be discussed in the Epilogue). It thus provides many other options for attractive segments. The other factor that has to be considered along with the attractive force is the physical features of the attractive segment. The attractive force is not the only property that the attractive segment should yield. It also should bring its own physical properties, which are eventually factored into the assembled system.

Self-assembly takes place because an attractive force from an attractive segment is balanced with a repulsive force from a repulsive segment. Hence, the next step is the identification of a proper repulsive segment. Table 1-1 also lists typical repulsive segments. As for the attractive segments, the choice of the repulsive segments is not limited to those in the table. The first criterion for the repulsive segment is the balance with the attractive segment. Its strength and working range should be comparable with those of the attractive segment so that it can be balanced at a certain point of the attractive process. Second, it should satisfy its own physical properties. Just like the attractive segment, once the repulsive segment is incorporated into the building unit, it will have an intrinsic impact on the properties of the

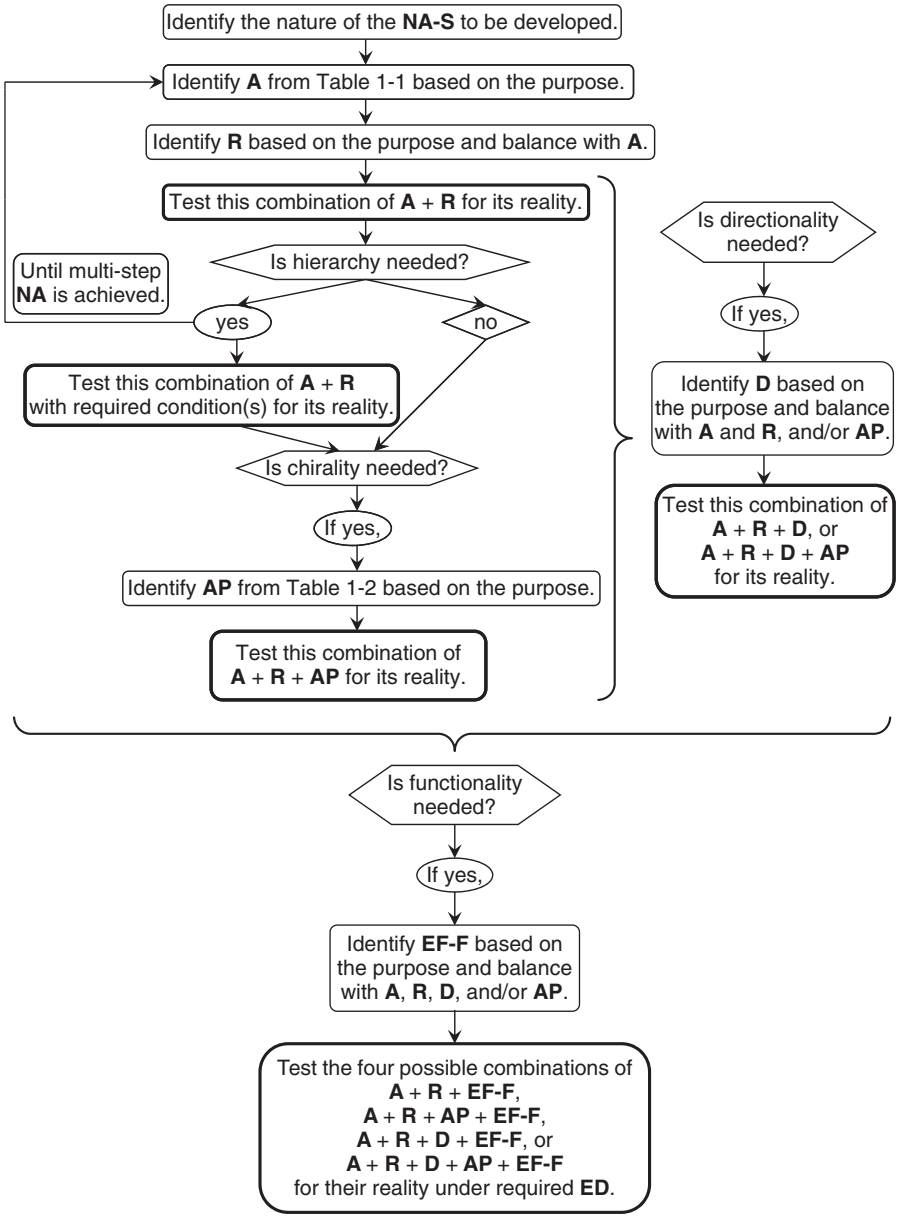

Identify the nature of the **NA-S** to be developed.
Identify **A** from Table 1-1 based on the purpose.
Identify **R** based on the purpose and balance with **A**.
Test this combination of **A** + **R** for its reality.
Is hierarchy needed?
Until multi-step **NA** is achieved.
yes
no
Test this combination of **A** + **R** with required condition(s) for its reality.
Is chirality needed?
If yes,
Identify **AP** from Table 1-2 based on the purpose.
Test this combination of **A** + **R** + **AP** for its reality.
Is directionality needed?
If yes,
Identify **D** based on the purpose and balance with **A** and **R**, and/or **AP**.
Test this combination of **A** + **R** + **D**, or **A** + **R** + **D** + **AP** for its reality.
Is functionality needed?
If yes,
Identify **EF-F** based on the purpose and balance with **A**, **R**, **D**, and/or **AP**.
Test the four possible combinations of **A** + **R** + **EF-F**, **A** + **R** + **AP** + **EF-F**, **A** + **R** + **D** + **EF-F**, or **A** + **R** + **D** + **AP** + **EF-F** for their reality under required **ED**.

Figure 10-1. General overview of the design of nanoassembly systems whose assembled systems show intrinsic functionalities. **A, R, D, AP**, and **EF-F** refer to attractive, repulsive, directional, asymmetric packing, and external force–specific functional segments, respectively. **ED** is external force–induced directional factor. **NA** and **NA-S** are short for nanoassembly and nanoassembled system, respectively.

assembled system. These include the sizes/morphologies of the assembled systems and the subsequent factors of the assembly. The subsequent factors here mean the capability of multi-step assembly and those that should be considered when there is a requirement for heterogeneous assembly (for more about heterogeneous assemblies, see Chapter 7). Once a repulsive segment is determined, the combination of the attractive and repulsive segments should be tested for its reality as an assembly building unit. This means to confirm whether it indeed shows assembly capability. The general overview, schematic illustrations, and examples in Chapter 3 should be helpful for this.

The third question is about hierarchy. If the nature of the assembly system requires a morphological hierarchy when the assembled system is formed, the combination of the attractive and repulsive segments from the previous steps should have the capability of multi-step assembly. Chapter 4 has the details on this. If it turns out that there is not enough capability for multi-step assembly, then we should go back to the first step. Another attractive segment that can meet this new requirement can be considered. But the difficulty is that the physical properties of the first-chosen attractive segment should be satisfied as well. If the choice of attractive segment is changed, the choice of the repulsive segment should also be modified accordingly. Then, the new combination of attractive and repulsive segments should be tested. This cycle should be repeated until it shows a multi-step assembly capability. Chapter 5 has the guidelines for the structure determination of the assembled systems. And Chapter 6 shows how the morphological hierarchy of assembled systems can be designed.

The fourth question comes with the chirality that is the other key morphological characteristic of assembled systems. If by any reason the assembled system requires chirality, then the building unit under design should have an asymmetric packing segment or the assembly system should be under the conditional factor that can induce asymmetric packing. Table 1-2 has typical examples. The possibilities for asymmetric packing segments go beyond those in the table. The same argument is valid for the choice of asymmetric packing segments as for the attractive and repulsive segments. They first should have clear capability to induce asymmetric packing when the building units assemble. At the same time, the asymmetric packing segment often becomes a critical part of the building unit so that it can express important physical properties such as spectroscopic ones. These properties are not just from the assembled systems. Those during the assembly process are equally important in many cases. One thing that can be useful for the selection of asymmetric packing segments is that biological systems have a particularly rich spectrum of asymmetric packing natures. Many possibilities can be found from them. The core logic of the bio-mimetic systems is to mimic the crucial characteristics of biological systems. Once a proper asymmetric packing segment is identified and incorporated into the combination of attractive and repulsive segments, this new combination, now having three segments, has to be put to the test for its reality. Two key requirements have to be met. The first one is assembly capability, and the second one is the capability of asymmetric packing. Chapter 6 shows the details for the chirality of the assembled systems.

The next step is for directionality. Directionality arises when the assembly is pointed in a certain direction by segments other than the attractive, repulsive, or asymmetric packing segments. The result of a directional assembly is always associated with the deformation or directional growth of the aggregates from those assembled without directionality. This is mainly generated by a directional segment. Therefore, if the answer to that question is yes, there is a requirement for directionality, then a proper directional segment has to be identified. Table 1-1 lists typical examples. The first criterion for a directional segment is that it should have the capability to direct the assembly process. It also should satisfy the balance with the attractive and repulsive forces, with or without the asymmetric packing segment. This is why the diagram for directionality is separated from the main one in Figure 10-1. A directional segment is also, in many cases, a crucial component that determines the capability of multi-step assembly and the physical and chemical properties of the aggregates. Some examples include the mechanical rigidity of aggregates, the permeability of the aggregates with linear structures, and the activity of bio-aggregates. These factors have to be considered during the selection of directional segments. Once selected, the combination of attractive and repulsive segments either with the directional segment or with both the directional and asymmetric packing segments should be tested for its reality. Chapter 3 has the details on the impact of directional segment on assembly capability. Chapters 5 and 6 provide the details on its impact on the structures and morphological characteristics of the aggregates.

The final question is for the functionalities that are responsive to external signals. Again, the functionalities of assembly systems are expressed not only by the aggregates but by the assembly processes as well. Intrinsic functionalities of assembly systems are usually expressed by the aggregates formed up to this step. However, some of the intrinsic functionalities are often synergistically improved when they properly cooperate with external signal–responsive functionalities. Thus, if the answer to this question is yes, then a proper external force–specific functional segment should be selected. Chapter 9 described all the details about this. It also examined external force–induced directional factors that work along with the functional segments. The functional segment should be susceptible to the change in the specific external signal. At the same time, it should not significantly perturb the force balance with the other segments. Once the functional segment is determined, the four possible segmental combinations (the final box in the diagram) should be tested for their reality.

10.3. ASSEMBLY PRINCIPLES

Figure 10-2 is the schematic illustration of the design of nanoassembly systems whose assembled systems show intrinsic functionalities. It shows that functional building units can be designed through the rational combination of the five assembly segments (for details about each assembly segment, see Figures 1-3 and 1-5). As described in the previous section, this always begins with the selection of an

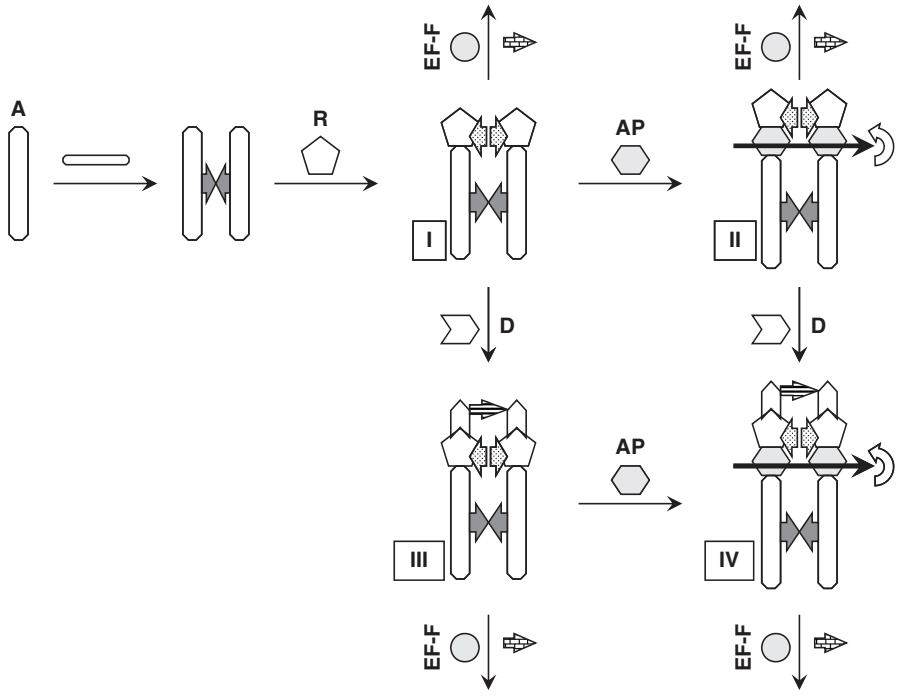


Figure 10-2. Schematic explanation of the design of nanoassembly systems whose assembled systems show intrinsic functionalities. **A, R, D, AP**, and **EF-F** refer to attractive, repulsive, directional, asymmetric packing, and external force–specific functional segments, respectively.

attractive segment, followed by the selection of a repulsive segment. The combination of these two segments makes the first building unit, which is referred to as *assembly system I*. An asymmetric packing segment can be combined with this combination whenever necessary. This is *assembly system II*. The location of the asymmetric packing segment strongly affects the actual degree of asymmetric packing. This is another important factor to consider when an asymmetric packing segment is positioned. Its location in the scheme is in between the attractive and repulsive segments. This does not mean that an asymmetric packing segment has to be always at this position. It can vary according to its purpose. As shown in the separate diagram in Figure 10-1, a directional segment can be combined with either system I or II. The one combined with system I is *assembly system III*, and the one combined with system II is *assembly system IV*. Assembly system IV can also be obtained by the addition of an asymmetric packing segment to assembly system III. As with the asymmetric packing segment, the location of the directional segment in the diagram is just for brevity. Its actual location can be anywhere within the building unit. And it should be logical, too, because even a small change in its location can sometimes have a big impact not only on the assembly process but on the possible synergistic or antagonistic effect on the other segments as well. This possibility is more likely with the asymmetric packing segment in assembly

system IV. An external force–specific functional segment can be combined at any stage of the design.

10.3.1. Molecular Assembled Systems

Figure 10-3 shows the design of functional molecular/bio-mimetic assembly systems. For example, it is assumed that their assembled systems seek three intrinsic functionalities. The first one is a small value of *cmc* (critical micellar concentration). This is to minimize their amounts in a real application so that they can maximize its efficiency. A strong thermal (or hydrothermal) stability of their assembled systems is the second functionality. This is to increase their effectiveness when they are applied under harsh conditions. The third one is the strong possibility to form a nanostructured gel (hydrogel or organogel). A nanostructured gel with the other two functionalities can have diverse applications, including functional materials, functional nanoscale devices, and templates for secondary functional materials. The notations with capital letters parallel those in Figure 10-2.

Figure 10-3(a) illustrates the design steps. It involves three fundamental segments and an asymmetric packing segment. The first step is selection of an attractive segment. Perfluorinated dodecyl carbon chain is chosen for this example. This chain provides enough attractive force through the hydrophobic interaction. In fully fluorinated form it actually generates a higher degree of attractive force compared with its hydrocarbon analog. This can ensure the likelihood of lower *cmc* value. A greater attractive force with the same repulsive force almost always induces more favorable assembly, which should be reflected in a lowered *cmc* value. In addition, it is well known that fluorocarbon chain has better hydrothermal stability than hydrocarbon chains. Thus, it can satisfy the second functionality as well. This is why the amphiphiles widely used in fire extinguishers are largely based on fluorocarbon chain derivatives.

The second step is for the repulsive segment. For this example, polyethylene oxide–based group, which is nonionic, is selected. Compared with ionic groups, this group counterbalances the strong attractive force with a somewhat lower degree of repulsive force and thus can decrease the *cmc* value even further. Amphiphiles with nonionic head groups are also more environmentally benign. *Assembly system I* is the combination of these two segments.

The third step is to add an asymmetric packing or directional segment to assembly system I. A gluconate-based sugar group is chosen for the asymmetric packing segment, and an amide group is chosen for the directional segment. This sugar group has a high degree of asymmetric packing capability due to its multiple numbers of asymmetric packing segments. This could minimize the possibility that the strong attractive force generated by the fluorocarbon chain will unnecessarily overtake its asymmetric packing.

This sugar group also could yield additional functionality by providing a molecular environment that is friendly to biological or bio-mimetic activities. This can actually reinforce the third functionality. The same benefit can be expected from the amide group. Furthermore, a relatively small size of the amide group could ensure minimum interference in the force balance between the attractive and

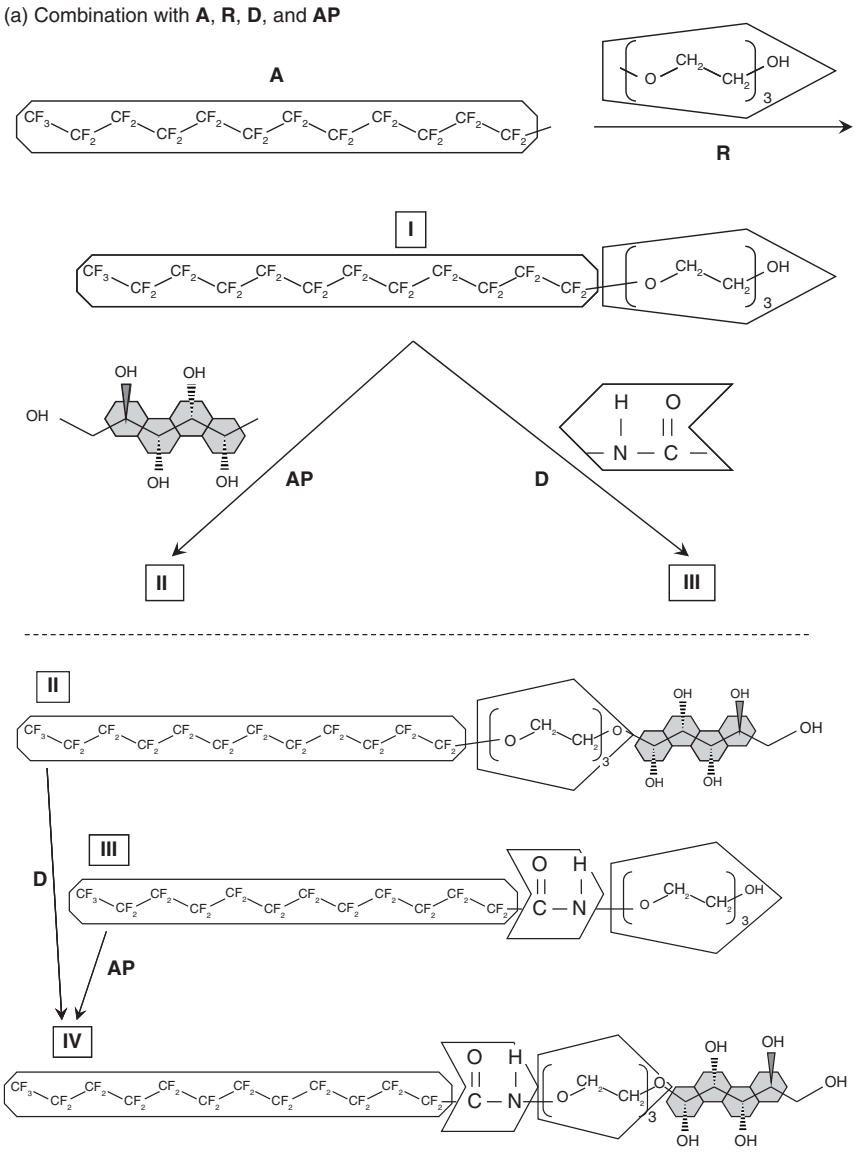
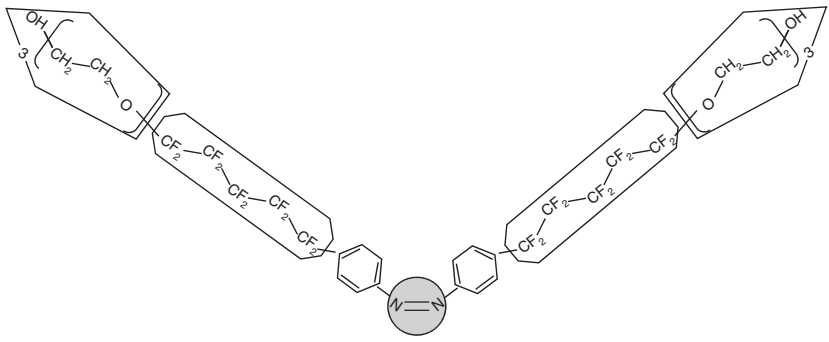


Figure 10-3. Design of molecular/bio-mimetic assembly systems whose critical micellar concentrations (*cmc*) are relatively small and whose assembled systems have a good thermal stability with a strong possibility of nanostructured gel formation. **A, R, D, AP**, and **EF-F** refer to attractive, repulsive, directional, asymmetric packing, and external force–specific functional segments, respectively.

(b) Combination with **EF-F**: e.g., incorporation of azobenzene group within I



EF-F

Figure 10-3. *(Continued)*

repulsive segments. *Assembly systems II and III* are the combination of this asymmetric packing and directional segments with assembly system I, respectively.

The location of each segment within the building units is also logical. The asymmetric packing segment is relatively big. Thus, if it is placed in between the attractive and repulsive segments, it might interrupt their force balance. If it is placed at the other end of the attractive segment, it might reduce the attractive force. For the amide group, this interruption might be much lower than the sugar group.

The last step is the combination of all selected segments. This is *assembly system IV*. It is obtained either by adding the directional segment to assembly system II or by adding the asymmetric packing segment to assembly system III. A strong attractive force combined with a weak repulsive force that is equipped with strong directional and asymmetric packing forces can ensure multi-step assembly, which can eventually bring ordered gels with useful morphological characteristics.

Lastly, all of the assembly systems that are designed here are conceptual ones. The segmental analyses strongly suggest that all of them will self-assemble under well-controlled conditions and yield the expected intrinsic functionalities. But that needs to be confirmed through an actual synthesis and characterization.

Figure 10-3(b) combines an external force–specific functional segment with assembly system I. Let us here assume that we want a building unit that is sensitive to light. The azobenzene group is the most typical candidate for this. Let us also assume that we want to carry the thermal stability. A fluorocarbon-based attractive segment is chosen again for this. Noticeably, the chain length is rather short for this fluorocarbon. This is to prevent the overwhelming attractive force from complicating the action of the azobenzene group. The same nonionic repulsive segment is chosen as for Figure 10-3(a). Ionic repulsive segments might work well, too. However, they might also conflict with the action of the azobenzene group. Once again, this is a conceptual structure. But the segmental analysis suggests that it will self-assemble in aqueous solution and be functional under ultraviolet or visible lights.

Case Study 10.1

The design of peptide amphiphiles (Cui et al., 2010) is an excellent example of the rational design of functional molecular self-assembly building unit. Peptide amphiphiles are a class of molecules that possess the self-assembly capability with the bioactive peptide groups. Their design covers five assembly segments. The purpose of the design is to achieve two main functionalities: the nanofiber morphology of assembled systems that can be woven into further network structures and their biocompatibility. An attractive segment is selected first, which is a long hydrocarbon chain. It will induce an attractive hydrophobic force and thus ensure the assembly. A charged group is selected next. This is a repulsive segment that will ensure the proper balance with the attractive segment. It can also ensure that the final building unit will have enough solubility in water. The next segment the authors chose is the short peptide sequence. Peptides even with short lengths have multiple asymmetric packing segments along with multiple directional segments that almost always trigger the formation of assembled systems with fibrous morphologies. The first functionality can be achieved with incorporation of this segment. It also induces chirality within the β-sheet region. Bioactive epitope group is selected as the fifth segment. This group can interact with biological cells or proteins, thus making the external force–specific functional segment of this building unit. The location of each segment is also very logical. By attaching the attractive segment and the functional segment on the opposite ends of the building units, they can ensure that the inactive hydrocarbon chains can be buried inside the nanofiber while the bioactive epitope group can be located on the surface of the nanofiber. In terms of the schematics in Figure 10-2, these peptide amphiphiles belong to assembly system IV with functional segments. Their further studies showing the independence of the asymmetric packing segments from the attractive or repulsive segments are also very intuitive regarding the application of segmental analysis. This article also reviews a diverse range of recent applications of self-assembled peptide amphiphiles as cell scaffolds, drug carriers, bioactive networks for central nervous system regeneration, angiogenesis, and regeneration of bone and enamel.

Case Study 10.2

The rational design of low-molecular-weight hydrogelators (de Loos et al., 2005) so that their self-assembled hydrogels can express diverse functionalities is another excellent case study for this section. Their design begins with the hydrophilic and hydrophobic parts, which are the repulsive and attractive segment, respectively, to fine-tune the balance between these two parts. This can ensure that the designed self-assembly building units (hydrogelators) have the self-assembly capability. In addition to this attractive–repulsive force balance, anisotropic and directional assemblies are another primary prerequisite for the functional hydrogelators. A number of diverse groups that have multiple asymmetric packing segments along with multiple directional segments are designed

and, as expected, shown to be effective for the formation of functional hydrogels. In terms of the schematics in Figure 10-2, these hydrogelators also belong to assembly system IV, but without clear functional segments.

Case Study 10.3

Multi-compartment micelles are self-assembled aggregates of low-molecular-weight or polymeric amphiphiles, which are composed of a hydrophilic shell and phase-separated incompatible compartments of the hydrophobic core. The strategies shown in Lutz and Laschewsky (2005) to achieve such assembled systems also begin with the rational design of their building units. To obtain bi-compartment core systems, two different hydrophobic units, one hydrocarbon and one fluorocarbon, are selected first. Both of these are attractive segments. A hydrophilic unit, which is the repulsive segment, is then selected and polymerized with the two attractive segments. These belong to assembly system I in Figure 10-2. One of their potential primary applications is the selective entrapment and release of diverse compounds such as drug molecules, independently of each other.

10.3.2. Colloidal Assembled Systems

Figure 10-4 shows the design of functional colloidal assembly systems. The intrinsic functionality is assumed to be a thermally sensitive magnetorheological fluid. The notations with capital letters parallel those in Figure 10-2.

The first step is selection of the right attractive segment. Iron oxide nanoparticle can be a reliable choice because of its ferromagnetic property, which is intrinsic. van der Waals force provides an attractive force with enough strength, thus becoming an attractive segment for this nanoparticle. A simple surface treatment can ensure the formation of surface charge, which can counterbalance the attractive force. This surface charge is its repulsive segment. The combination of these two segments is *assembly system I*. This is a symmetric assembly system, which means that its aggregates will likely have globular morphologies. This can ensure well-dispersed, homogeneously at least at a length scale larger than the particle, aggregates in a given liquid. This fluid (colloidal sol) becomes sensitive on external magnetic field as a new force induced by the ferromagnetic property of the nanoparticle under magnetic field is working *with* or *against* the attractive and repulsive forces.

The next step is to identify an asymmetric packing or directional segment and add it to assembly system I. Because of their sizes, colloidal building units have somewhat limited choices for these two segments compared with molecular ones. But many of the typical examples from Tables 1-1 and 1-2 work well as for molecular building units when they are chosen carefully and placed in a way that is comparable to the sizes of colloids. One of the most effective ways to create an asymmetric packing for colloidal building units is with an asymmetric morphology of the building unit itself. As an example and to be consistent with the discussion in Chapter 5 (Figure 5-6), an iron oxide nanoparticle that has a hexagonal prism morphology with an asymmetric cut on one of its corners is chosen. This can

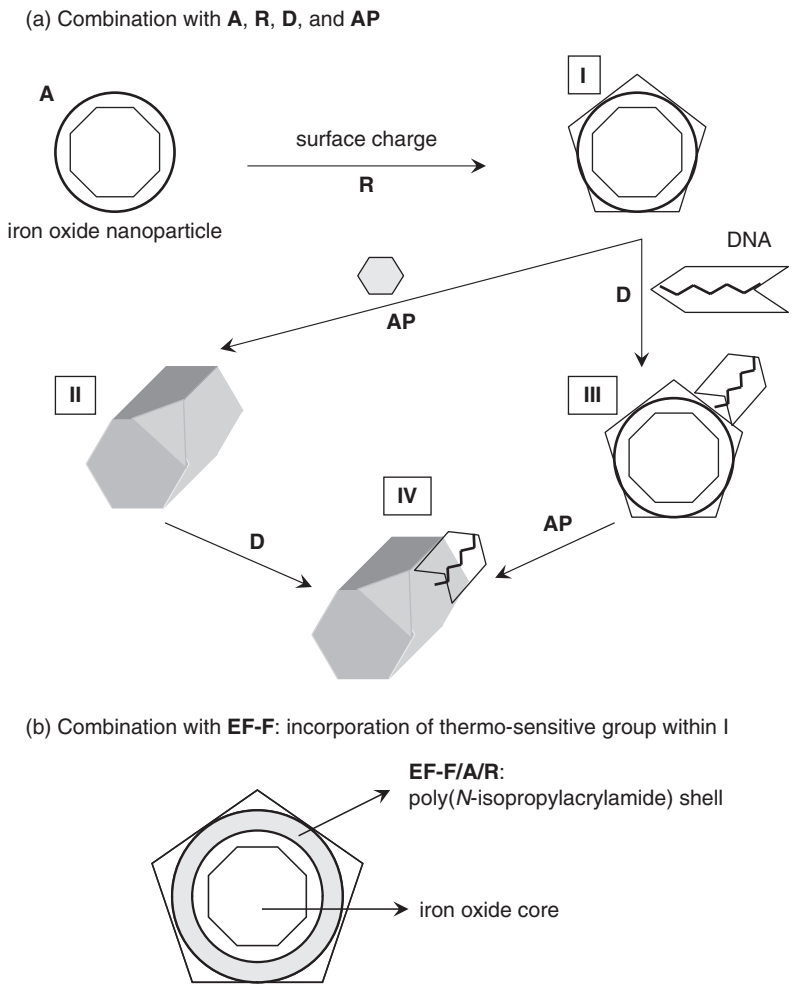


Figure 10-4. Design of colloidal assembly systems whose assembled systems become thermally sensitive magnetorheological fluid. **A, R, D, AP**, and **EF-F** refer to attractive, repulsive, directional, asymmetric packing, and external force–specific functional segments, respectively.

ensure an asymmetric assembly and the formation of asymmetric aggregates. Under magnetic field, the force balance change in this asymmetric aggregate will be much stronger than that in symmetric aggregate. This in turn promotes stronger expression of magnetorheological property. This is *assembly system II*. With the same reasons as for the asymmetric packing segment, DNA is selected as the directional segment. Incorporation (more appropriately, attachment on the surface of the particle) of this directional segment into assembly system I makes *assembly system III*. Due to its nature, DNA works not only as a powerful directional segment but as an attractive segment as well. This induces more favorable assembly and larger aggregates. The last step is to combine all of the selected segments into one building unit. This

gives a hexagonal prism-shaped nanoparticle whose surface is cut asymmetrically and decorated with DNA chains. It will self-assemble asymmetrically under proper conditions. And the DNA chains offer an additional control for the morphology of its aggregates. This is *assembly system IV*.

The selection of an external force–specific functional segment and its combination with other segments are shown in Figure 10-4(b). Thermal sensitivity is another functionality we are seeking here. Figure 9-8 showed the thermo-sensitive assembly of poly(*N*-isopropylacrylamide) particles in water at room temperature. Also, the assembly mechanism indicated that the same thermo-sensitivity should be expressed in other aqueous solutions, too. This polymer is known to be stable over a wide range of temperatures that might be critical for its applications at different temperatures. It thus becomes a safe choice for the functional segment. How to add this segment to the combination of the attractive and repulsive segments brings up another technical point. When making this building unit thermo-sensitive, the location of this polymer might not make much difference as long as it is placed on the surface of the iron oxide nanoparticle. However, it makes technically more sense when the polymer covers the entire surface of the nanoparticle. It might be also possible to attach the polymer on a specific part of the surface. But that would not be very practical as far as this functionality is concerned. This creates iron oxide-poly(*N*-isopropylacrylamide) core-shell type of nanoparticle. The attractive segment (van der Waals force from the nanoparticle) now has an additional contribution from the polymer, and the repulsive segment is almost solely from the polymer. This segmental structure suggests that it will self-assemble in aqueous solution and the favorability of the assembly will vary below and above 33 °C. A reverse core-shell type of the nanoparticle, that is, poly(*N*-isopropylacrylamide) as a core and iron oxide as a shell of the nanoparticle, is also practically relevant. Based on its segmental structure, it will self-assemble with magnetorheological property. However, this type of nanoparticle will certainly lose almost all of its thermo-sensitivity because of its structural constraint.

As with those in the previous section, all five colloidal building units designed here are conceptual ones. Their segmental structures strongly suggest that all of them will self-assemble under proper conditions and generate the intrinsic functionalities. But this must always be confirmed through experiment.

Case Study 10.4

The design of laterally tethered nanorods (Nguyen and Glotzer, 2009; 2010) is a good example of a rational design of colloidal assembly building units. These nanorods form switchable helical self-assembled aggregates by hierarchical self-assembly in solution without any confinement effects. An attractive van der Waals force between rods or between tethers brings the nanorods together, thus making their attractive segment. For a repulsive segment that balances this attractive segment, a repulsive van der Waals force that is simulated by changing the solvent selectivity with either rods or tethers is used. The authors varied the volume fractions of rod and tether parts and the relative strength of interactions between rods and tethers in a systematic manner. The combined effects

of these two factors makes the asymmetric packing segment of the nanorods. Thus, these nanorods belong to assembly system II in Figure 10-2 without any functional segment. Spontaneous formation of helical self-assembled aggregates of colloidal particles and their reversible morphological transformations shown in these studies provide excellent insights for the assembly of switchable nanomaterials that have many interesting potential applications, including fine-tuning of nonlinear optical properties and waveguide devices.

10.4. FROM ASSEMBLED SYSTEMS TO NANOMATERIALS

As for the external signal–responsive nanomaterials shown in Section 9.5, one of the key issues in practice for the materializing of nanomaterials with intrinsic functionalities is how to achieve this step without losing the functionalities of each assembled system. There is no reason why the four common situations in which most of these nanomaterials should function should be different from those for external signal–responsive nanomaterials. Thus, the second paragraph of Section 9.5 is generally valid for nanomaterials with intrinsic functionalities. A simple scale-up of selected assembled systems is usually enough to obtain the desired nanomaterial. In addition, since these nanomaterials are materialized mainly through the scale-up of assembled systems, instead of the scale-up of assembly processes as is the case for the external signal–responsive nanomaterials, it is less likely that they will lose their functionalities during the materializing process.

10.5. COLLECTION OF NANOMATERIALS WITH INTRINSIC FUNCTIONALITIES

Table 10-1 collects the nanomaterials that have intrinsic functionalities. Intrinsic functionalities are mainly expressed by the assembled systems or the changes in assembled systems rather than the changes in the assembly processes. Each of the functionalities is the unique result of each assembly system. And, for almost all of them, the key is the correct design of their building units. The building units should have the exact structural, physical, or chemical properties that are necessary for the functionalities. These key aspects are shown in the second column of the table. The assembly process/system in the third column shows the common terms that appear in the literature for each of the functionalities. For example, when syntheses that take place in organic solvents are placed under the right aqueous micellar solutions, those syntheses can be induced in aqueous solution. During the synthesis, this in turn could reduce the usage of organic solvents that are usually harmful to the environment. Also, when the reactants of a certain synthesis are selectively localized on a confined space of the right assembled system, its reaction rate probably can be greatly enhanced. For both types of studies, the term *micellar solubilization* is commonly used to track their molecular mechanisms. For another example, when a solid surface is selectively functionalized through surface assembly of well-designed building units, it can provide the ability to control the transport behaviors of certain molecules or particles. This is an important

TABLE 10-1. Collection of nanomaterials that have intrinsic functionalities.

Functionality	Key to the Functionality	Assembly Process/system	Application
reaction rate	localized/selective solubilization	micellar catalysis, micellar phase-transfer catalysis	synthesis of nanomaterials, tertiary oil recovery, green synthesis
		micellar solubilization	drug delivery, cosmetics
catalysis	structural control	nanoparticles, nanofilms, nanopores	heterogeneous catalysis, solar cells, batteries
bio-comparability	membrane mimicry	model membrane	lipid monolayer/bilayer to mimic biological membranes
		model biological cell	vesicular systems for bio-functionality
		bio-inspired assembly	development of bio-mimetic functionalities
	geometrically matching hetero-assembly	biomineralization	synthesis of nanomaterials, bio-kinetics, polymorphism
separation	interfacial adsorption/aggregation	micellar-enhanced ultrafiltration	soil remediation, waste-water treatment, ground-water cleanup
drag-reducing	rapid assembly/disassembly/reassembly	flexible micellization	crude oil transport, heating/cooling system
environmental susceptibility	intermolecular force	selective switching of intermolecular/colloidal force[1]	micro-/nano-manipulation for nanofabrication
transport	surface self-assembly	functionalized surfaces	fluidic devices, chromatography
controlled growth	geometrically matching homo-assembly	crystallization	synthesis of nanomaterials, polymorphism
gelation	multi-step assembly	entanglement and networking of micelles	drug delivery, cosmetics, soft nanomaterials

[1] Dejeu et al., 2009.

functionality for many modern technologies, including micro-/nano-fluidic devices and chromatography. The most typical applications for each of the functionalities are also shown. But the applications are certainly not limited to those in the table.

10.6. SUMMARY

As already mentioned in Section 7.1, before we became serious about sustainability, science and technology developed as if the main focus was on the usefulness and convenience of the end products. The result, in many cases, was the introduction of them into the market without proper and well-regulated examination of the potential harms. In many cases, the problems cropped up later and then we had to struggle to deal with them. But the environmental and societal damage already had been done. Reducing wastes while improving energy efficiency will make more sense by finding and removing the potential side effects before the products go into the market. The output-oriented design of assembly systems shown in this chapter can be one way to obtain better efficiency for many nanotechnology systems while reducing unnecessary wastes. This chapter showed that:

1. Intrinsic functionalities of many nanomaterials can be rationally designed.
2. This takes the right design of functional assembly systems, and the right path to assemble them into nanomaterials.
3. The building units for functional assembly systems can be rationally designed by first selecting each segment based on the desired functionality and then combining them together as a building unit based on the key aspects of their assembly.

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11

Nanostructures: Designed to Perform

11.1. NANOISSUE

Structure and property aspects of nanotechnology systems can be classified into four main categories: nanostructure, nanoproperty, nanofabrication, and nanodevice/nanomachine. We have to assemble proper nanostructures first so that we can reveal nanoproperties. These nanostructures and nanoproperties then have to be networked to bring integrated functions into reality. This is nanofabrication. Finally, they have to be devised such that they are capable of communicating with the macroworld. These are nanodevices and/or nanomachines. This chapter examines the first issue, nanostructures.

The diversity of nanostructures may appear limitless. However, almost all nanostructures can be actually classified as nanopore, nanoparticle, or nanofilm. Any specific nanostructure belongs to one of these three categories. More complicated or hierarchically structured ones can be expressed through combinations of any two or three of them. For a quick example, nanoislands can be viewed as the combination of nanoparticles with nanofilms. To this end, the main issue of this chapter is:

> *How can the most effective nanoassembly system be designed for an individual nanostructure?*

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This leads to the following questions:

How can the most effective nanoassembly route be designed to integrate multiple nanostructures into one?

What are the general rules between the nanoassembly building units?

Inevitably, the discussion in this chapter is closely related to the issues of nanoproperty, nanofabrication, and nanodevice/nanomachine, which will be examined in the next three chapters.

11.2. GENERAL OVERVIEW

Figure 11-1 is a general overview of the design of nanoassembly to assemble the three different types of nanostructures (for details on nanoassembly, see Section 2.1). The three separate branches represent each type of nanostructure. It begins with the distinctive roles of self-assembly and self-assembled aggregates (for the relation of self-assembly to nanoassembly, see Section 2.6), combined with those overviews developed in the previous chapters.

The first step is to identify what type of nanostructure is necessary for a given purpose. If the nanopore-based nanostructure is the one to be developed, the self-assembled aggregate (*aggregate* for short) for the assembly system has to be

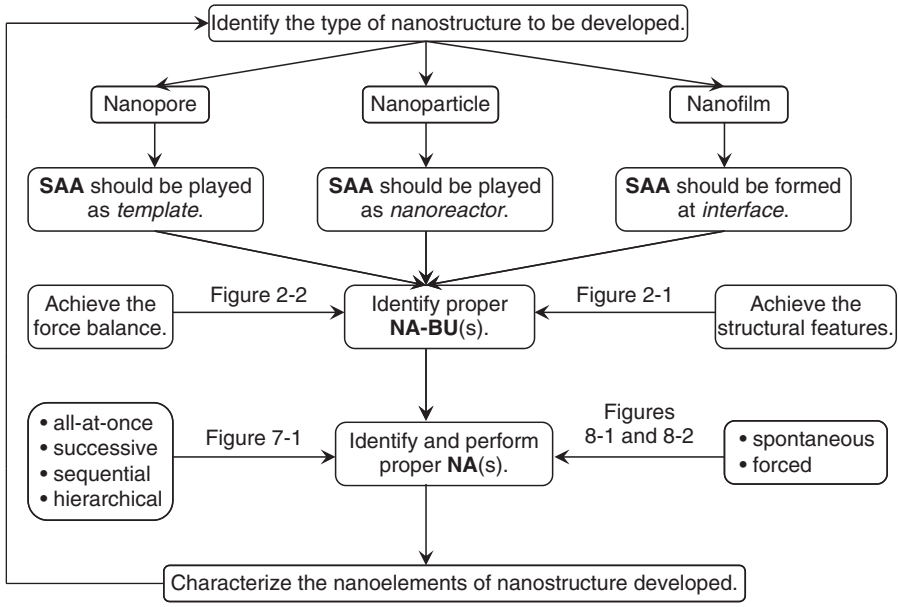


Figure 11-1. General overview of the design of nanoassembly (**NA**) to assemble different types of nanostructures. **SAA** refers to self-assembled aggregate. **NA-BU** is short for nanoassembly building unit.

designed as a *template*. This means that the aggregate almost always has to be assembled at the very beginning of the assembly, and it has to have the capability of providing the nanoscale space that can accommodate the subsequent assembly process around it. It also has to have enough structural integrity because the assembly often takes place under harsh conditions. At the same time, it has to be easily removed from the system after the completion of the assembly. As will be seen later, most aggregates, which mostly have organic or biological origin, are surprisingly stable and flexible enough to satisfy these requirements.

If the nanoparticle-based nanostructure is necessary, the aggregate has to be designed as a *nanoreactor*. This concept is almost exactly the opposite of *template*. The aggregate still has to be assembled at the beginning of the assembly. However, it has to have the capability of providing the nanoscale space where it can contain or restrict the subsequent assembly process. It also has to have enough structural integrity. At the same time, it has to be flexible so that it can release the nanoparticle after the completion of the assembly. As in the nanopore cases, most organic and biological aggregates satisfy these requirements. For both cases of *template* and *nanoreactor*, colloidal aggregates, which are usually harder than those from organic or biological counterparts, also meet these requirements. But they often bring the opposite issue of being too sturdy to be used for the assembly of nanostructures. This problem will be discussed later in this chapter.

For the nanofilm-based nanostructures, the roles of surfaces and interfaces become critical. Aggregate should be formed at surfaces or interfaces at the beginning of the assembly. It should promote the subsequent assembly on its surfaces and guide it in a certain direction. The need for structural integrity and flexibility is also important here.

Proper building units should be identified next. Since the building units that form the aggregates are eventually removed for all three types of nanostructures (unless they become a part of the nanostructures), these building units are the ones that make the nanostructures. Two criteria should be considered in making the selection. They should satisfy the force balance and they must have the structural features that can properly express the sizes of the nanostructures. Figures 2-1 and 2-2 provided the details for these. The next step is to identify the proper assembly route/mode. Figure 7-1 showed how to choose either the all-at-once, successive, sequential, or hierarchical mode. Figures 8-1 and 8-2 showed how to identify spontaneous or forced assembly routes. The nanoelements (for details, see Section 2.3) of each nanostructure have to be characterized upon the completion of the assembly. If they do not satisfy the given purpose, the process should go back to the first step.

11.3. ASSEMBLY PRINCIPLES

11.3.1. Analysis of Building Units

Figure 11-2 shows the nanoassembly building units (for details, see Section 2.2) that are used for the assembly of the nanostructures shown in the chapter. Their segmental structures are also shown (for details on segmental analysis, see Subsection 1.2.2). The symbols for each type of building unit are from Figure 2-1. To

be consistent with previous chapters, rectangular and circular symbols are used for molecular and colloidal building units, respectively.

Figure 11-2(a) has five self-assembly building units. The first four of them are homologue series and the last one is a phospholipid. For the alkyltrimethylammonium bromides and alkylpyridinium bromides, their segmental structures are essentially the same regardless of their hydrocarbon chain length. This is the case as long as they are soluble in a given solution. The hydrocarbon chain provides

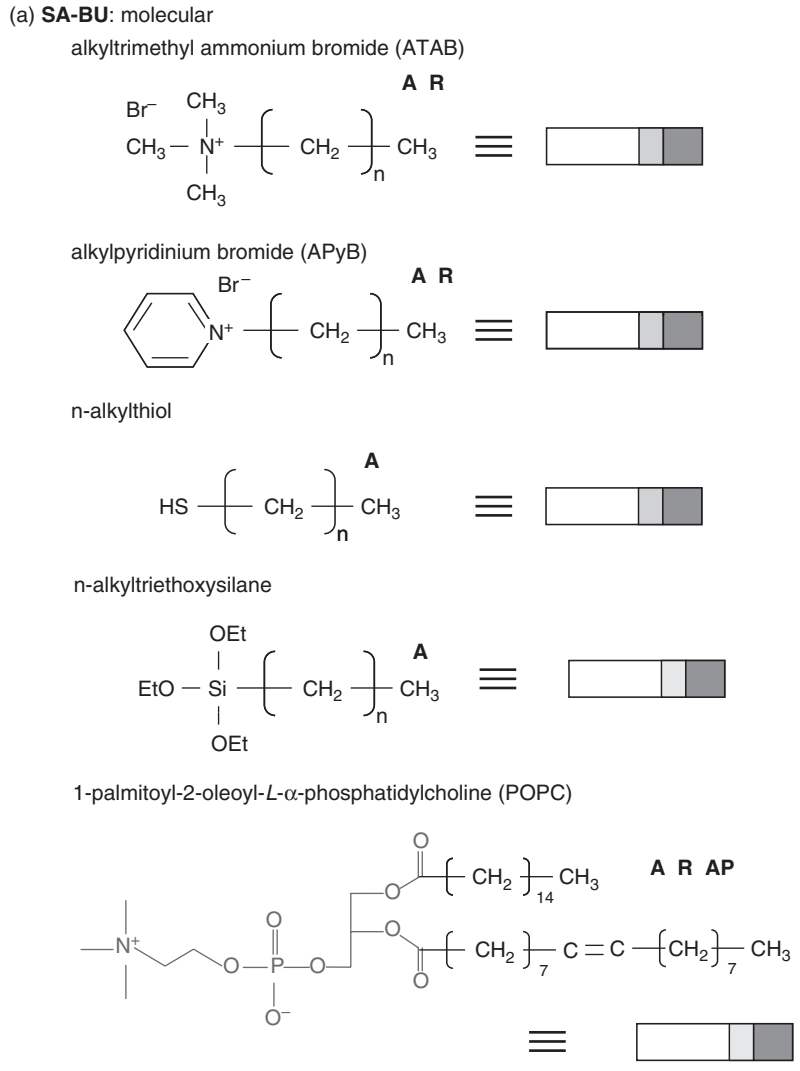
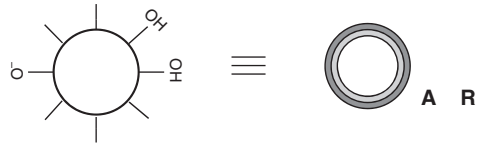


Figure 11-2. Building units. **SA-BU, F-BU**, and **R-BU** refer to self-assembly, fabrication, and reactive building units, respectively. **A, R**, and **AP** refer to attractive, repulsive, and asymmetric packing segments, respectively.

(b) **SA-BU**: colloidal

polystyrene (PS) colloidal particle with minimal surface charge

silica colloidal particle with natural surface silanol group



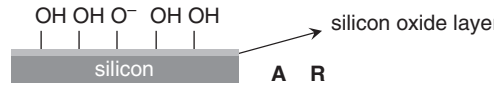
(c) **SA-BU**: substrate

silicon

highly oriented pyrolytic graphite (HOPG)

(d) **F-BU**

silicon substrate with oxidized surface layer



(e) **R-BU**

germanium vapor

silver vapor

tetraethyl orthosilicate (TEOS)

chloroauric acid

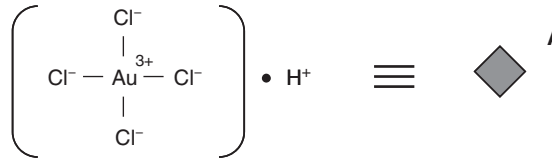


Figure 11-2. (*Continued*)

the attractive hydrophobic force, thus becoming their attractive segment. The ionic, both cationic, head groups are their repulsive segments because they induce electrostatic repulsive force. The other two series are alkylthiols and alkyltriethoxysilanes. Their overall molecular structures are similar to those of the first two. Both have long hydrocarbon chains that should become their attractive segments because of their ability to generate the attractive hydrophobic force. Some differences, however, come from their head groups. Both thiol and triethoxysilane groups can be reactive. The thiol is especially reactive when it meets with noble metals such as gold and silver. The triethoxysilane becomes highly reactive when it meets with specific oxide surfaces such as silica, and at the same time it is reactive each other. This could lead us to see alkylthiols and alkyltriethoxysilanes as a reactive building unit. But they retain their structural features after the assemblies, and their attractive segments, unlike the ordinary reactive building units, play a significant role in the force balance between them and with other building units. This means that they are quite reasonably viewed as a self-assembly building unit. And then it is logical to assign both the thiol and triethoxysilane groups as other attractive segments. These are typical examples where the attraction, which is always the first step for the assembly, could occur through the reactive process but not through intermolecular interaction.

The last building unit is 1-palmitoyl-2-oleoyl-*L*-α-phosphatidylcholine (POPC). Its molecular structure is very similar to 1,2-dipalmitoyl-*L*-α-phosphatidylcholine (DPPC), shown in Figure 5-4. The only difference is in their hydrocarbon chains. One of the hydrocarbon chains of POPC is the bulkier oleoyl group. Both chains of DPPC are linear. But both types of the chains can generate an attractive hydrophobic force. Thus, the two hydrocarbon chains of POPC should have no problem being assigned as its attractive segment. The rest of the molecular structure of POPC is the same as that of DPPC. Both have one chiral carbon and their head groups are the same phosphatidylcholine group. This means that the head group and the chiral carbon of POPC become its repulsive and asymmetrical packing segments, respectively.

Figure 11-2(b) shows two colloidal building units. Polystyrene colloidal particle is assumed to have minimal surface charges. This suggests that this particle has only an attractive segment while its repulsive segment becomes negligible. Silica particle is assumed to have natural surface silanol groups. This causes it to have both attractive and repulsive segments.

Figure 11-2(c) shows the substrates that can be viewed as a self-assembly building unit. In Chapters 7 and 8, the substrates were not classified as any type of building unit. This was mainly because they were not significantly related to the nanoissues of those chapters. For this chapter, however, by viewing the substrates as a self-assembly building unit, their assembly with other building units can be described more practically. Two solid substrates are shown. They are silicon and highly oriented pyrolytic graphite (HOPG). Just like the colloidal particles, both have the capability to generate van der Waals force, which is their attractive segment. For both, it is assumed that there are neither natural surface charges nor any types of functional groups attached on their surfaces. This makes them have no or negligible repulsive segments.

In Figure 11-2(d), the surface of the silicon self-assembly building unit is modified with an oxidized thin layer. This oxidized thin layer gives it surface silanol groups. The actual degree of the protonation or deprotonation of the silanol groups is dependent on the solution conditions. However, they provide a repulsive force for this substrate. They can also become a reactive site depending on the nature of other building units. van der Waals force, as with the solid substrate self-assembly building units in Figure 11-2(c), is its attractive segment.

Figure 11-2(e) shows four reactive building units. The first two are germanium and silver vapors. The same logic as for the gold vapor in Figure 7-2(c) can be applied to these two. Both metal vapors should be viewed as a reactive building unit with attractive segment only. Tetraethyl orthosilicate and chloroauric acid are commonly used for the assembly of silica-based and gold-based nanostructures, respectively. Tetraethyl orthosilicate, in aqueous solution, goes through hydrolysis and condensation during assembly. For chloroauric acid, it is usually decomposition followed by nucleation and growth. For almost all cases, only the attractive force is operative during these processes, which gives them only an attractive segment.

11.3.2. Nanostructure Assemblies

Figure 11-3 presents how self-assembly works for the assembly of different types of nanostructures. Three assemblies are shown in parallel. The same two building units, cetyltrimethylammonium bromide (CTAB) and tetraethyl orthosilicate (TEOS), are used for all three.

For all three assemblies, let cetyltrimethylammonium bromide self-assemble in aqueous solution first. It has both attractive and repulsive segments. Thus, this is a typical symmetric assembly that forms spherical aggregates. But the first difference between the different types of nanostructures comes from here. By assembling this building unit in well-designed solution conditions, three distinctively different types of aggregates can be obtained, which in turn can be used for the next steps of the assemblies. When the solution is made of water or water-based mixtures, the force balance between cetyltrimethylammonium bromide molecules becomes the way that their hydrocarbon chains are embedded inside the aggregate while their charged head groups stay outside of it. By separating the nonpolar parts of the building units from water and causing the polar parts to make contact with water, this assembly generates a thermodynamically stable aggregate. This is a normal micelle. On the other hand, when the solution is made of oils with a trace amount of water or of oil-based mixtures, the force balance occurs in such a way that their hydrocarbon chains attract each other, and at the same time contacting with oil-phase. The repulsive force operates only in the presence of water. The amount of oil is dominant over water. And the formation of a film-like region where this force balance pushes water to the edge of the oil phase is unrealistic because there is no way that the force balance between the attractive and repulsive segments becomes perfectly symmetric. Formation of water droplets that are encircled by the assembled cetyltrimethylammonium bromide molecules is the only energetically possible outcome. This is a water-in-oil microemulsion or reverse micelle. When,

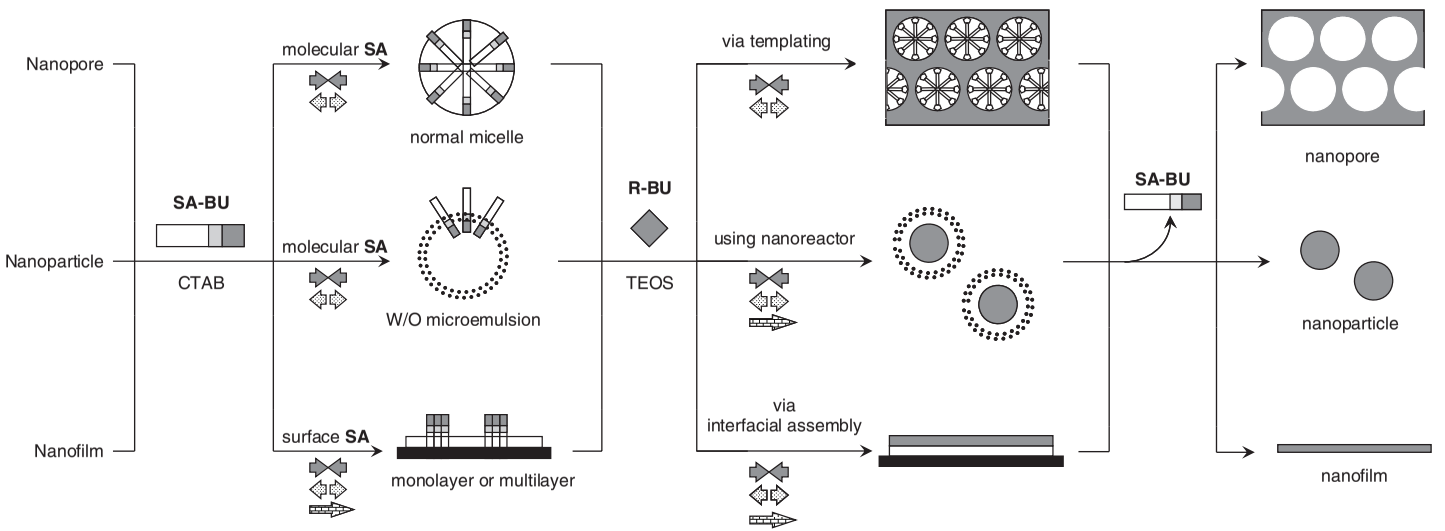


Figure 11-3. General comparison of the roles of self-assembly (**SA**) in the assembly of different types of nanostructures. **SA-BU** and **R-BU** refer to self-assembly and reactive building units, respectively.

for the third assembly, cetyltrimethylammonium bromide molecules are placed on a hydrophobic surface, and the assembly is well-controlled to maximize the attractive interaction between their hydrocarbon chains and the surface, the surface aggregate can be obtained with a form of monolayer or multilayer. This will be the case as long as their concentration is high enough. (Hemimicelle will be a more likely form for the aggregate if their concentration is slightly above the surface *cmc* [critical micellar concentration]). All three assemblies are spontaneous. And the first two are typical molecular self-assembly and the third one is surface self-assembly with its directionality induced by the surface.

The three different types of aggregates can now be used as *template*, *nanoreactor*, or *interfacial* aid for the next steps. The second building unit (tetraethyl orthosilicate) is added to each of the aggregates. Once hydrolyzed, its only attractive segment shows a strong attractive interaction with the charged head groups of cetyltrimethylammonium bromide. For the normal micelle, this leads it (hydrolyzed tetraethyl orthosilicate) to be attracted to the outer surface of the micelle. For the water-in-oil microemulsion, this pushes it inside the microemulsion where water is located. For the surface aggregate, this interaction attracts the hydrolyzed tetraethyl orthosilicate on its surface. All three assemblies are spontaneous. For the second one, the spatial confinement is imposed by the aggregate; thus it is a directional assembly. The same is true for the third one, but its directionality is provided by the two-dimensional nature of the aggregate. Upon the completion of silica condensation, composites of cetyltrimethylammonium bromide with silica are formed for all three assemblies.

The last step is to remove cetyltrimethylammonium bromide molecules from the composites. This results in silica nanopore for the first assembly, silica nanoparticle for the second one, and silica nanofilm for the third one. The aggregates of cetyltrimethylammonium bromide were a template creating the nanopore inside bulk silica, a nanoreactor making the silica into the nanoparticle form, or an interfacial aid producing the silica film. For all three nanostructured silicas, nanostructural element (for details, see Section 2.3) should be the primary nanoelement to be characterized, which is done to confirm whether they show the designed morphology having a proper size. Depending on the removal techniques, such as solvent or supercritical fluid extraction, cetyltrimethylammonium bromide molecules can often be collected and purified for reuse.

11.3.3. Nanopore-Based Nanostructures

This subsection describes the assemblies of nanopore-based nanostructures. Figure 11-4 depicts typical assemblies. This figure is designed to show that seemingly different assemblies can be understood as one unified process despite the differences in their building units. As long as the aggregates work as *template*, they should have little trouble coming up with nanopore-based nanostructures.

The first step is to have a well-developed aggregate. The sizes of the nanopores are directly correlated with the sizes of the aggregates. The shapes of the nanopores are directly determined by the shapes of the aggregates. And the arrangements

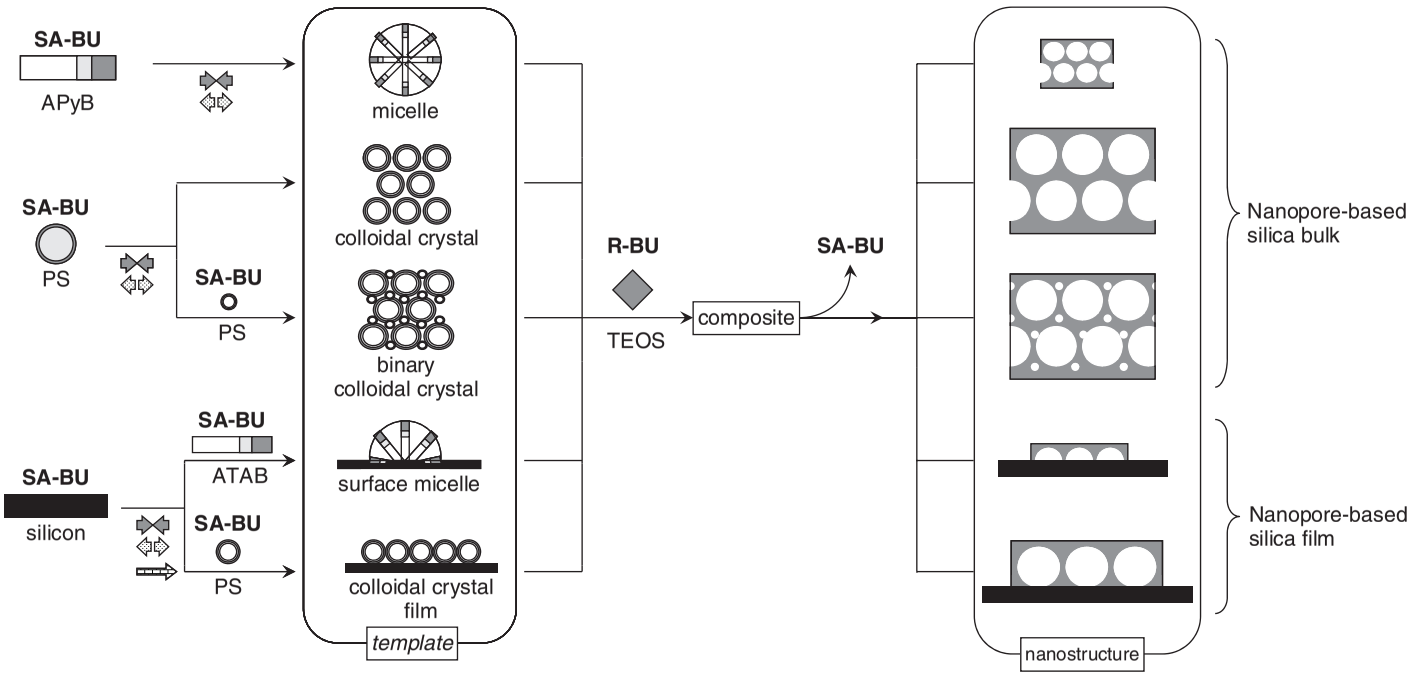


Figure 11-4. Assembly of nanopore-based nanostructures. **SA-BU** and **R-BU** refer to self-assembly and reactive building units, respectively.

of the nanopores are also directly determined by the arrangements of the aggregates. If the sizes of the aggregates are increased in a systematic manner, the sizes of the nanopores are increased accordingly. If the aggregates are binary systems with two different sizes, the nanopores become binary systems with two different pore sizes. To show these relations clearer, different types of building units are used in the figure. For molecular building units, alkylpyridinium bromide homologue series self-assembles into cationic micelles through the force balance between their attractive and repulsive segments. For colloidal building units, polystyrene particles (with enough surface charges for this example) form a colloidal crystal. If polystyrene particles of two different sizes are used, a binary colloidal crystal will be formed. These are the second and third aggregates in the rounded rectangle that contains all of the aggregates that work as *template*. Figures 7-3(a) and 7-4(a) have more details on these assemblies. The next two aggregates are formed on silicon surface with alkyltrimethylammonium bromide homologue series and polystyrene particles. Let us assume at this time that the aggregates of alkyltrimethylammonium bromides are surface micelles. Then, they should be hemimicelles, considering the hydrophobic nature of silicon. Polystyrene particles form a colloidal crystal film.

The next step is to assemble the reactive building unit with each of the aggregates. Tetraethyl orthosilicate is used for all five. As stated in the previous subsection, this building unit hydrolyzes in aqueous solution. It is then attracted to the surface of the aggregates or to the interstitial regions of the aggregates. This is through the attractive interaction between the attractive segment of the aggregates (charged group or region) and the attractive segment of tetraethyl orthosilicate. (The attractive segment of the aggregates means the part of the aggregates that can generate the attractive interaction with the reactive building units, i.e., hydrolyzed tetraethyl orthosilicate. It does not imply the attractive segment of the building unit that forms the aggregates.) Careful control of solution pH would be necessary to ensure this attractive interaction. Lastly, let the hydrolyzed tetraethyl orthosilicate be condensed. For all five aggregates, this produces composites of the aggregates with silica. A removal of the aggregates from the composites results in pores at the places where the aggregates had been located. The sizes of the aggregates are in the nanoscale, thus the sizes of the pores are in the nanoscale as well. The first three are nanopore-based silica bulks. The second two are nanopore-based silica films. Usually, those obtained from colloidal aggregates have larger nanopores than those from molecular aggregates.

Figure 11-5 shows how to control the four key nanostructural elements (pore size, pore morphology, pore arrangement, and pore hierarchy) that define the nature of nanopore-based nanostructures. The horizontal arrow on top depicts the control of pore size. With possible overlap, the sizes of the aggregates are increased from surfactant micelle to polymer micelle, microemulsion, macroemulsion, and to colloidal crystal. This is in other words increasing the size of the *template* in this direction. Unless the structures of the aggregates are considerably varied during assembly (this often happens with some reactive building units), the sizes of the nanopores are increased in this direction as well. The vertical arrow on the

left-hand side depicts the control of pore morphology (or morphological diversity). The morphological diversity of nanopores can be achieved only through the direct structural changes in the aggregates. A force balance between attractive and repulsive segments primarily determines the structure of the aggregates. However, whenever there is a force rebalance (whether it is intrinsic or extrinsic), the aggregates respond accordingly by changing their structures. This leaves no option but to change the pore morphology as well. A greater more degree of force rebalance generally induces more diverse pore morphologies. The vertical arrow on the opposite side of the figure depicts the control of pore arrangement. Pore arrangement means the degree of long-range alignment of nanopores. Since the force balance within the assembly system causes an almost predetermined degree of alignment between its aggregates, this control for the pore arrangement has to take advantage of the additional forces that can make the assembly more directional. This can be achieved by adding a directional segment or by choosing forced assembly (for details on forced assembly, see Chapter 8). More directionality generally yields more aligned nanopores unless the additional force reaches the point where it begins to disrupt the entire assembly. The last structural element is pore hierarchy. Its control can be achieved on the two-dimesional space laid out by the three arrows. Through the combinations of any two or three of the elements (pore size, pore morphology, and pore arrangement), the nanopores have a good possibility of being hierarchical. This means that the nanopores consist of two or more different structural elements. These include different sizes, different morphologies, different arrangements, different sizes with different morphologies, different morphologies with different arrangements, and more. For this control, the assembly

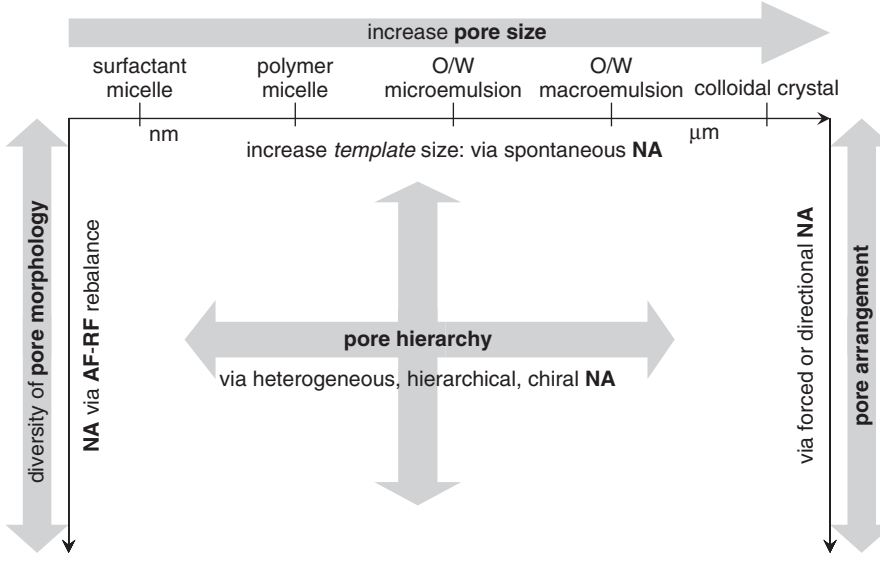


Figure 11-5. Control of the key nanostructural elements of nanopore-based nanostructures. **AF** and **RF** refer to attractive and repulsive forces, respectively. **NA** is short for nanoassembly.

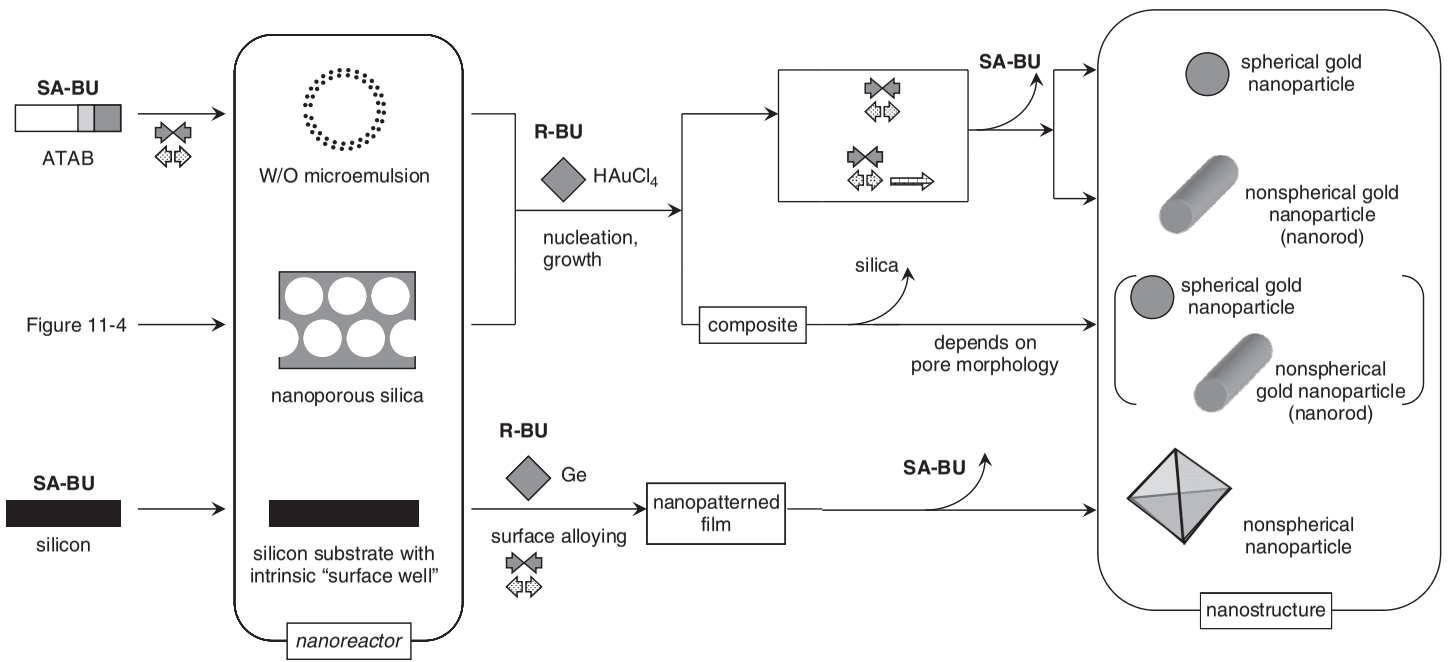
would need to take heterogeneous, hierarchical, or even chiral routes (for details on these assembly routes, see Chapter 7). A book edited by Lu and Zhao (2004) provides a general overview for the synthesis, functionalization, characterization, and applications of nanoporous materials.

11.3.4. Nanoparticle-Based Nanostructures

Figure 11-6 shows the assemblies of nanoparticle-based nanostructures. As with the nanopores in Figure 11-4, different assemblies can be understood with one unified process despite the differences in their building units. As long as the aggregates work as *nanoreactor*, they should be able to come up with nanoparticle-based nanostructures.

This figure illustrates three different self-assembly building units. The first one is alkyltrimethylammonium bromides, which has well-defined attractive and repulsive segments. As explained for cetyltrimethylammonium bromide in Figure 11-3, in oil-based solvents, they usually form a water-in-oil microemulsion. Its water droplet, which has the nanoscale size, is the nanoreactor. The second building unit is the nanoporous silicas from Figure 11-4. The nanopore itself is a nanoreactor for the next steps. The third one is silicon. Even though this silicon is assumed to have its average surface roughness below or around the nanoscale, it usually has a geometrical inhomogeneity that is regularly dispersed on its surface. For many assemblies, this can be used as a "surface well" that confines the subsequent building units within, on, or around it. It does not have a clear-cut three-dimensional boundary like the other two building units, but it can well limit the further assembly of the building units within the nanoscale. These three are the nanoreactors shown in the rounded rectangle.

While the nanoreactors provide the geometrical constraint, it is the reactive building unit that determines the compositions of the nanoparticles. Thus, the next step is to select a proper reactive building unit and assemble it within, on, or around the nanoreactors. For the first two assembly systems, chloroauric acid is used. This is because the gold nanoparticle is intended to be obtained from them. Germanium gas is chosen for the third system. The reason is the same. It is the germanium-based nanoparticle that is intended here. When chloroauric acid assembles inside the water-in-oil microemulsion or inside the silica nanopore under aqueous solution, it first goes through nucleation and then grows. Chloroauric acid has an attractive segment only, and it does not have any significant attractive interaction with either alkyltrimethylammonium bromide or silica unless the condition is specifically designed for it to do so. Thus, the attractive interaction inside the nanoreactors mainly occurs between chloroauric acids. This attractive interaction is counterbalanced when the growth reaches the point where the boundary of the nanoreactors physically limits their further growth. This is not exactly a typical attractive interaction that is counterbalanced by a repulsive segment. However, in the sense that it is also a physical interaction–driven balance, not driven by strong bonds, this can be also understood within the scope of the force balance between assembly segments (for details on the concept of force balance, see Sections 1.1 and 2.1).


SA-BU
ATAB
W/O microemulsion
Figure 11-4
nanoporous silica
SA-BU
silicon
silicon substrate with intrinsic "surface well"
nanoreactor
R-BU
HAuCl4
nucleation, growth
R-BU
Ge
surface alloying
nanopatterned film
composite
silica
depends on pore morphology
SA-BU
SA-BU
spherical gold nanoparticle
nonspherical gold nanoparticle (nanorod)
spherical gold nanoparticle
nonspherical gold nanoparticle (nanorod)
nonspherical nanoparticle
nanostructure

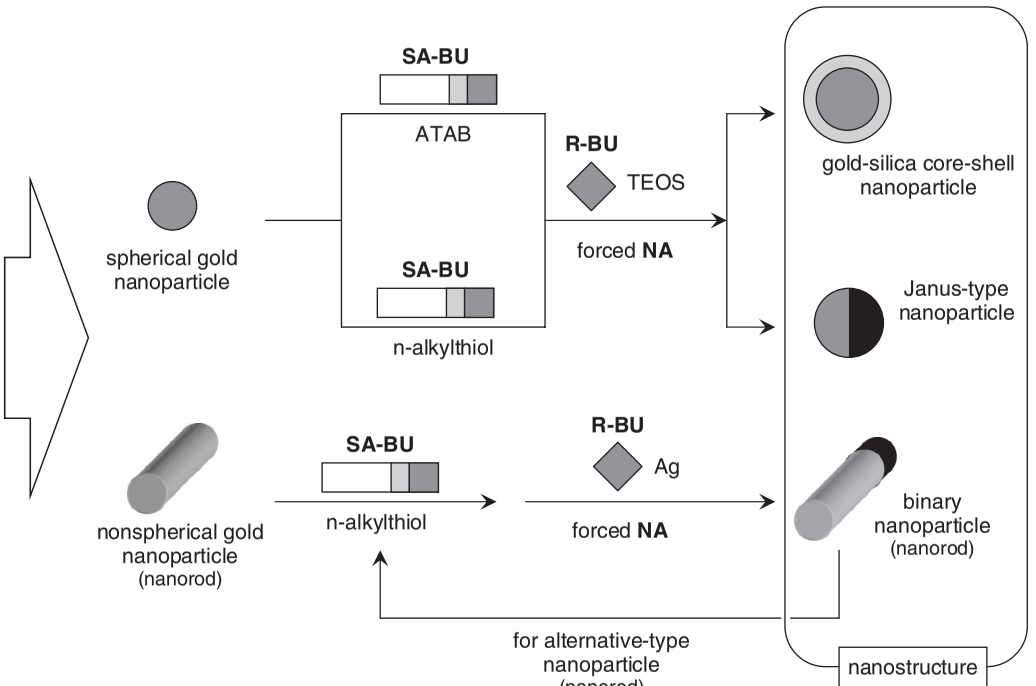


Figure 11-6. Assembly of nanoparticle-based nanostructures. **SA-BU** and **R-BU** refer to self-assembly and reactive building units, respectively. **NA** is short for nanoassembly.

The nucleation and growth of the reactive building unit (chloroauric acid) within water-in-oil microemulsion can be typically promoted via two different routes. The first one is letting it happen with the force balance for microemulsion keeping its symmetric nature. The second one is also letting it happen but with the force balance for microemulsion being changed into an asymmetric one. When the force balance is symmetric, the formation of gold nanoparticle becomes symmetric, too. This makes spherical or close-to-spherical gold nanoparticles. The asymmetric force balance makes this step asymmetric. And its result is usually nonspherical gold nanoparticles. For the nanoporous silica, when chloroauric acid is nucleated and grown, the first outcome is a composite of silica with gold. This composite itself could be a useful nanoassembled system with promising potential. To obtain gold nanoparticles, the silica part has to be removed from the composite. The morphology of gold nanoparticles is directly determined by the morphology of the silica nanopore. Not only spherical nanoparticles but nonspherical nanoparticles as well, including nanorod or nanowire, can be produced at this step. Germanium gas is a reactive building unit for silicon. It is attracted onto silicon through van der Waals force. However, this attraction is stronger on the areas where the silicon surface is geometrical inhomogeneous because the surface energy on these areas is much higher than the rest of the surface. This causes the incoming germanium atoms to be selectively attracted onto these areas until the geometrical constraint (the sizes of the area of inhomogeneity usually are in the nanoscale) counterbalances the attraction. Since this assembly takes place within this constrained area, the effect of surface as a directional force will be minimal. Therefore, this assembly is close to a symmetric force balance, and results in the mixing of germanium atoms with silicon atoms, which is actually surface alloying. This step generates nanopatterned germanium on silicon surface. It might also be called nanopatterned film. The germanium/silicon structure here is called a *nanoisland*. If the self-assembly building unit (silicon) can be removed without harming the nanoisland, nonspherical nanoparticle whose composition is germanium/silicon can be obtained.

Case Study 11.1

The synthesis of hierarchical nanostructures of lead sulfide nanowires with helically rotating epitaxial branches is reported by Bierman et al. (2008). This work very clearly shows how an asymmetric assembly works for the formation of morphological hierarchy and chirality of nanoassembled systems. The screw component of an axial dislocation on the surface of substrate is the critical factor for this. In terms of the segmental analysis, this screw component is an asymmetric packing segment for this assembly system. This propagates through all the steps of the assembly. The size of the screw component is estimated as ~6 angstroms. This segmental analysis becomes clearer when it is understood in conjunction with example IV in Figures 6-4 and 6-5, which describes the formation of surface higher-order aggregates having hierarchy and chirality.

Spherical and nonspherical (*nanorod* for short) gold nanoparticles can be used for further assemblies. With proper building units and assembly routes, their

structural diversity can be further expanded into hierarchical structures. First, the spherical gold nanoparticles are assembled with alkyltrimethylammonium bromides or alkylthiols. Tetraethyl orthosilicate is assembled next. By taking well-designed assembly routes, this can result in gold-silica core-shell nanoparticle or Janus gold nanoparticle. The key to this assembly would be forced assembly, especially for the Janus gold nanoparticle. There is a comprehensive review article (Jiang et al., 2010) that provides more details of the synthesis of Janus nanoparticles and their assemblies. For the gold nanorod, sequential assembly (for details, see Figure 7-1) with alkylthiol and silver gas can assemble them into a binary type of nanorod. Forced assembly would be the key again in order to selectively modify the gold nanorod with the other building units. By repeating this assembly, the alternative type of gold-silver nanorod could be obtained. These derived nanoparticles could find rich applications, given their delicately controlled nanostructures.

Figure 11-7 shows how to control the five key nanostructural elements that define nanoparticle-based nanostructures. The horizontal arrow on top illustrates the control of particle sizes. As the nanoreactors are assembled from reverse micelle to surface well, water-in-oil microemulsion, nanoporous material, water-in-oil macroemulsion, and to inverse colloidal crystal, the sizes of the nanoreactors are increased accordingly. This is simply because the space that can take up the reactive building units inside of them is increased. Depending on the condition of each system, the size variation can be different. But with rare exceptions, larger nanoreactors generate larger nanoparticles. A typical spontaneous assembly is enough for this in most cases.

The vertical arrow on the left-hand side shows the complexity of particle structures. *Complexity* here means not only the diversity of nanoparticle structures but their degree of structural variation within each nanoparticle as well. This is somewhat different from the hierarchy in nanoparticle structures. This structural complexity arises as the force balance between the building units is disturbed and rebalanced. A greater degree of force rebalance could generally yield more complex structures. This force rebalance can be induced by either intrinsic or external factors.

The third nanostructural element is the directionality of nanoparticle structures. This is shown on the vertical arrow on the right-hand side. Directionality is mainly for nonspherical nanoparticles. It indicates how the length ratio of the long axis of nanoparticle to its short axis varies. Nanorod, nanowire, and nanotube are usually included in this. And they are usually assembled via a forced or directional assembly route. Greater directional force means that a greater degree of directionality can be expected.

The fourth nanostructural element is the polydispersity of nanoparticles. This element is defined regardless of the particle complexity and/or directionality, thus shown with the bottom horizontal arrow, in parallel with the arrow for the particle size. The control of stability and kinetic factors of nanoreactors is an important key for this element. Simply stated, a more stable nanoreactor during the assembly of reactive building units would provide more monodisperse nanoparticles. If the stability of nanoreactors varied constantly or if they had diverse sizes of

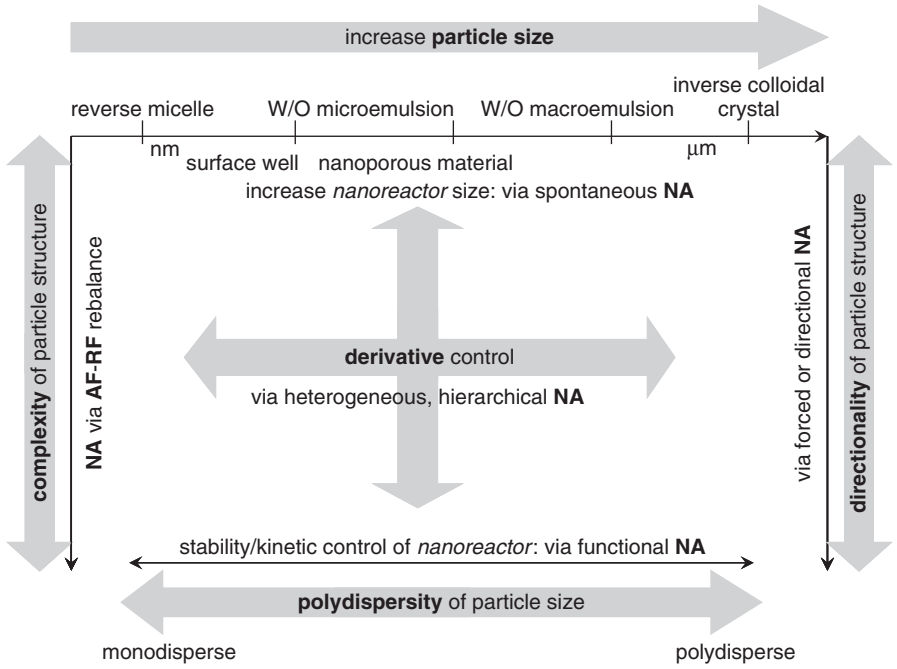


Figure 11-7. Control of the key nanostructural elements of nanoparticle-based nanostructures. **AF** and **RF** refer to attractive and repulsive forces, respectively. **NA** is short for nanoassembly.

nanoreactors in the first place, the outcome would be more diverse sizes of nanoparticles. This polydispersity control is closely related to the control of functional assembly.

Lastly, the derivative control of nanoparticle is about the control of its heterogeneity and hierarchy. The former is a compositional fact while the latter is a structural one. Whenever the nanoparticle is assembled to be composed of two or more chemically different components, it can be stated that its heterogeneity is controlled. And whenever the nanoparticle is assembled to have two or more different length scales, it can be stated that its hierarchy is controlled. While the control of the former four elements will have important impacts on the application of nanoparticles, this derivative control can drive their application potential into a whole new dimension. Heterogeneous and hierarchical assemblies usually work well for this. A book edited by Schmid (2010) provides a general overview of the syntheses, assemblies, and applications of nanoparticles.

11.3.5. Nanofilm-Based Nanostructures

Figure 11-8 shows the assembly of nanofilm-based nanostructures. As for the previous two subsections, different assemblies can be understood with one unified process. Once the aggregates are formed at surfaces or interfaces, there is a good chance that they can be used for the assembly of nanofilms.

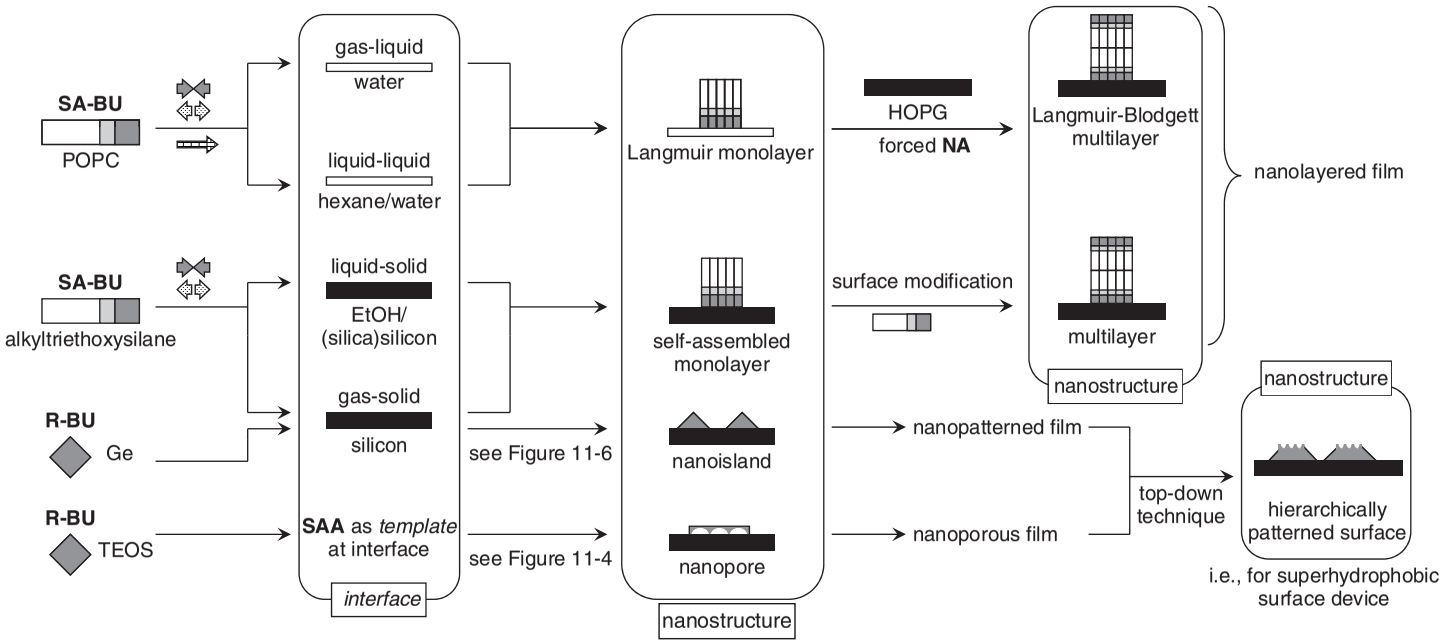


Figure 11-8. Assembly of nanofilm-based nanostructures. **SA-BU** and **R-BU** refer to self-assembly and reactive building units, respectively. **SAA** refers to self-assembled aggregate. **NA** is short for nanoassembly.

1-palmitoyl-2-oleoyl-*L*-α-phosphatidylcholine (POPC) is a typical building unit that has double hydrocarbon chains. Figure 11-2(a) showed that it has both attractive and repulsive segments. But the bulkiness of its attractive segment gives it extremely low solubility in aqueous solution. This suggests that it can easily assemble on the surface of aqueous solution without losing significant amounts of it into the solution, which makes it an ideal building unit that can take advantage of water-based interfaces for the assembly of nanofilms. This is the first building unit in the figure. The second one is alkyltriethoxysilane homologue series. As clarified in Figure 11-2(a), their attractive segment, which is actually reactive on certain types of solid surfaces, can make them a good building unit to assemble the aggregates on solid surfaces. The other two, germanium gas and tetraethyl orthosilicate, are reactive building units. For POPC, two water-based systems are used as an interface. One is the interface of water with its own vapor, and the other is hexane–water liquid–liquid interface. For alkyltriethoxysilanes, two solid substrates are used as an interface. The first one is silicon, whose uppermost surface is oxidized and contacted with ethanol, and the other one is pure silicon surface. A pure silicon surface is also used as an interface for both germanium and tetraethyl orthosilicate. These are the interfaces for the assemblies of nanofilms in the next steps.

Because of the low solubility in aqueous solution, once POPC molecules are placed on aqueous surfaces, most of them are dispersed and stay on the surfaces. The initial force balance between their attractive and repulsive segments on the surfaces likely gives their aggregates a lying-down mode. There is not enough force to make them have up-right mode (for details on the two different surface assembly modes, see Subsection 3.3.4). The aggregates with a lying-down mode have some usefulness for nanofilm assembly. However, it is usually the upright mode that finds a wider range of applications. Again, since there is no force from their segments that can make them be in the upright mode, it requires an external force to make this happen. Employing proper mechanical force can make this assembly. A lateral mechanical force along the direction of the surface can push the building units (POPC) closer. The attractive interaction between their attractive segments is certainly cooperative with this mechanical force. But the repulsive interaction between their repulsive segments is not. As the surface area that holds up the building units becomes smaller, the most favorable way to achieve the balance among all these forces is to have them be in upright mode. The combined attractive force of the mechanical force with the one from attractive segments compensates for the electrostatic repulsive force from repulsive segments, which, by the way, is increased exponentially as the distance between them is decreased by the mechanical force. The result of this force balance is Langmuir monolayer.

When the second building units, alkyltriethoxysilanes, are placed either on the surface of oxidized silicon or on pure silicon, their reactive attractive segments go through silanol condensation with the surfaces. The difference is mainly in how to deliver the building units on the surfaces. For the oxidized silicon, the building units can be solubilized in ethanol first, and delivered. For the pure silicon, they can be deposited in vapor form. For both cases, as long as there are enough building units that are making contact with the solid surfaces, the silanol condensation

causes them to be occupied on every possible silanol group site on the surfaces. And the attractive interaction between the alkyl chains of the building units helps them maintain an up-right mode. For this particular case, there are no intrinsic repulsive segments that counterbalance these attractive interactions. However, the predetermined (the surface is not limitless) area of the surface can be viewed as an external repulsive force here. The aggregates formed by this type of assembly are commonly called self-assembled monolayer (SAM).

The assembly of germanium/silicon nanoisland was shown in Figure 11-6.And the assembly of silica nanoporous film was shown in Figure 11-4.

The formation of proper aggregates on well-chosen surfaces was the key for all assemblies. This was mainly through spontaneous assembly, except for Langmuir monolayer, which was a forced assembly.

As in the previous subsection regarding nanoparticles, all of the nanofilms can be assembled further. For Langmuir monolayer, by using solid substrate (highly oriented pyrolytic graphite is selected here) with external mechanical force, it can be transferred onto solid substrates. Through different transfer modes (upstroke and downstroke), diverse types of multilayers can be assembled. This is called Langmuir-Blodgett film. Forced assembly once again is critical for this. A mechanical force is important to overcome the electrostatic repulsive force from the repulsive segments of the building units. For self-assembled monolayer, since reactive attractive segments are strongly bound on solid surfaces, additional surface modifications even under harsh conditions are possible without significantly interrupting its structural integrity. This opens up a facile way to functionalize its surface or build up additional layers with a wide range of building units, which otherwise would not be practical. These are the second set of nanofilms or nanolayered films, which are grouped in the third rounded rectangle. Given their stability and structural characteristics, there are diverse ranges of additional assembly options that can be explored for the third and fourth assembly systems. One example is using a top-down technique (such as sputtering or selective etching: details in Section 13.4) to produce hierarchically patterned solid surfaces. This second generation of nanofilm (the fourth rounded rectangle) can find very practical applications such as superhydrophobic surface devices.

There are five key nanostructural elements whose combinations define nanofilm-based nanostructures: number of layers, film thickness, surface roughness, surface pattern, and surface pore. Figure 11-9 shows how these elements can be controlled. The five elements are, in most cases, independent on the types of the interfaces where the nanofilm assemblies take place. The arrow on top represents four typical interfaces: gas–liquid, liquid–liquid, liquid–solid, and gas–solid interfaces. Their positions on the arrow are random, and do not have any specific implication for any changes in the key elements. A gas–gas interface is unrealistic. And solid–solid interface is not practical for the assembly of nanofilms. There could be some advantages to having nanofilm assembly at solid–solid interfaces. Some examples include interfacial alloying and a system that might require a specific process such as interfacial oxidation. However, most of the nanofilms that can be expected from solid–solid interfaces can be assembled at gas–solid interfaces more practically.

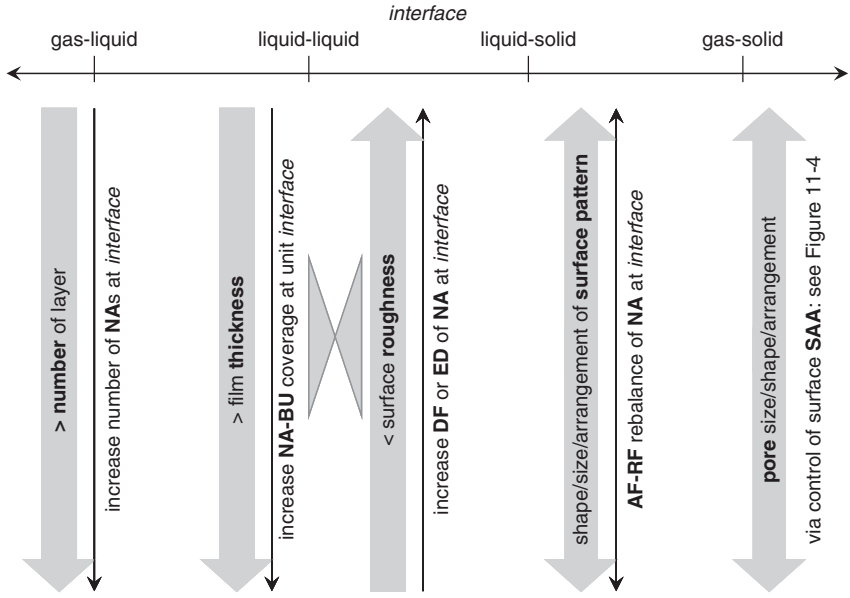


Figure 11-9. Control of the key nanostructural elements of nanofilm-based nanostructures. **AF, RF**, and **DF** refer to attractive, repulsive, and directional forces, respectively. **ED** is external force–induced directional factor. **SAA** refers to self-assembled aggregate. **NA** and **NA-BU** are short for nanoassembly and nanoassembly building unit, respectively.

The number of layers is primarily controlled with the number of assemblies at interface. If this is with the same set of building units, it becomes a successive assembly. If this is with different types of building units, it becomes a sequential assembly. Unless there is a significant rearrangement during and/or after the assembly, the number of layers is increased linearly with the number of assemblies.

A film thickness is primarily varied as a function of the amount of building units per unit area of interface. As the coverage of the building units is increased, the film thickness is increased almost linearly unless there is a significant conformational change within the building units. A typical example is the collapsing of long hydrocarbon chains.

The third key element, surface roughness, is in many cases strongly correlated with the film thickness. It is mainly governed by a directional force and/or external force. A greater degree of these forces causes the film to have a lower degree of surface roughness. However, their impact also reduces the film thickness unless the interface is well confined. And the opposite is true. Greater coverage for increased film thickness usually induces the film to have a higher degree of roughness. This is why the direction of the vertical arrow for the surface roughness is opposite to the first two vertical arrows. For assembly systems in reality, a logical combination of these two factors will always have to be carefully examined.

The next element, surface pattern, can embrace a much broader range of structural features. It includes the shapes of the structures that are patterned on

surfaces, the sizes of the structures, and their arrangement on surfaces. Intrinsic structural features such as surface defects, stepped surface structures, and surface reconstruction are also included for this element. In terms of assembly, the main factor that determines the surface pattern is the rebalance between attractive and repulsive forces at a given surface. A higher degree of force rebalance does not drive any of these specific structural features in any specific direction. And a lower degree of force rebalance does not drive any of them in any specific direction, either. However, a greater degree of force rebalance within a given assembly system will definitely provide a wider range of control for each of the structural features. This is expressed with the double-headed arrow in the figure.

Lastly, a nanopore control in nanofilms means control of pore size, shape, and arrangement. This can be achieved by controlling the aggregates at interfaces. Its details were shown in Figure 11-4. Unlike those in Figures 11-5 and 11-7, nanofilm controls do not provide a phase diagram–type of surface map that can help guide the actual assembly. But its rather independent characteristics for each key element can be useful when there is a necessity for independent control of a specific nanoproperty. This is actually the case for many nanofilms. A book edited by Kumar (2010) provides a general overview one the preparation, functionalization, and characterization of nanofilms.

11.3.6. General Trends

Figure 11-10 depicts a general trend of force balance in the assembly of three different types of nanostructures. As discussed throughout this chapter, the general

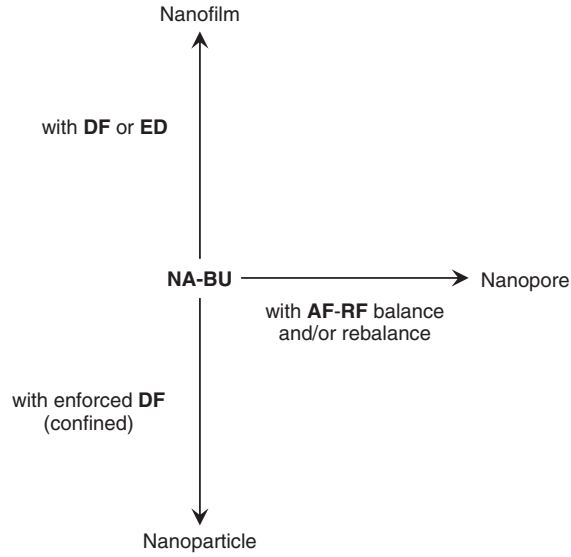


Figure 11-10. General trend of force balance for the assembly of three different types of nanostructures. **AF, RF**, and **DF** refer to attractive, repulsive, and directional forces, respectively. **ED** is external force–induced directional factor. **NA-BU** is short for nanoassembly building unit.

trends of nanostructure assemblies are quite independent of each other. Nanopores have their own general trend that can be used like a phase diagram. Nanoparticles also have a phase diagram–like general trend. The general trend for nanofilms has case-by-case functions. However, given the common sense that even the exact same set of building units can assemble into different nanostructures, a general picture for all nanostructures can also be suggested. With given building units, if the purpose is to obtain nanopores, then the design of the assembly primarily through the control of force balance (and/or rebalance) between their attractive and repulsive segments would bring much better results. For nanoparticles, the design of the assembly that focuses on a forced (more likely confined) directional force would mean a better chance for successful assembly. For nanofilms, a primary assembly design has to be focused on the control of directional and/or external forces. Depending on each assembly system, the actual control of force balance can be tricky. However, this overall assembly trend of the nanostructures can help us grasp their general assembly pictures and guide us in deciding which assembly route to take at the beginning of each assembly.

11.4. COLLECTION OF COMMON NANOSTRUCTURE NAMES

Table 11-1 lists the names that are commonly used for each type of nanostructure in the literature. Most of these names are based on the structural characteristics of each nanostructure. For example, when the number of building units, usually atoms, within the nanoparticle is defined, it is commonly called a *nanocluster*. When spherical or rod-shaped structures are emphasized, they are called *nanosphere* and *nanorod*, respectively. Some of them are named after their properties. A *quantum dot* is a semiconductor in nanoparticle form such that it confines electric charges in the nanoscale region, thus having discrete quantized energy levels.

11.5. COLLECTION OF NANOSTRUCTURES AND THEIR APPLICATIONS

Tables 11-2, 11-3, and 11-4 list the collection of each type of nanostructure. Table 11-2 has the nanopore-based nanostructures. Table 11-3 has the nanoparticle-based nanostructures. And Table 11-4 has the nanofilm-based nanostructures. As with the nanostructure names given earlier, these are the ones that appear frequently in the literature, but this is certainly not a complete collection. The physical and chemical properties that are induced, changed, or enhanced by each nanostructure are also shown. “Induced” indicates properties that are newly generated by a specific nanostructure. “Changed” indicates properties that already exist, usually in a microscopic or macroscopic region, but that evolve into different properties as the structures that have these properties enter the nanoscale. And “enhanced” implies that properties that already exist are improved by a specific nanostructure. Potential applications are also shown for all three types of nanostructures. Many interesting

TABLE 11-1. Collection of commonly used names for nanostructures.

Type	Nanostructure
nanoparticle	nanocluster
	nanosphere
	nanorod
	nanotube
	nanohorn
	nanowhisker
	nanopallet
	nanowire
	nanoneedle
	nanofiber
	nanobelt
	nanoribbon
	helical nanotube
	nanohelix
	nano screw
	nano-hollow sphere
	nanoring
	nanodisk
	nanocapsule
	nanoprism
	nanocube
	nanodendrite
	nanostar
	nanotree
	nano-tetrapod
	nanopowder
	quantum dot
	core-shell nanosphere
	Janus-type nanosphere
	alternative-type nanorod
	acorn-type nanorod
nanopore	nanochannel
	nanonetwork
	nanospace
	nanovoid
	nanocavity
	nanohole
nanofilm	nanosheet
	nanoplate
	nanolayered film
	nanocomposite film
	nano-free-standing film
	nanoisland

stories come out of these applications. For example, Table 11-4 shows frictional adhesion for hierarchically structured nanostructure solid surface. One interesting finding related to this frictional adhesion (Zeng et al., 2009) is that if the surfaces of our feet and toes were micro-/nanostructured like those of the Gecko, $\sim$230 cm^2 of total surface area would be enough to enable us to support ourselves on ceilings and walls just like Geckos do. Only van der Waals force is attributed to this estimation. This again reveals that even though van der Waals force (as well as

TABLE 11-2. Collection of nanopore-based nanostructures, their physical and chemical properties that are induced, changed, or enhanced by each nanostructure, and potential applications.

Nanostructure	Property	Potential Application
nanoconfinement (nanospace)	changes in viscosity, diffusion, phase behavior, structure, and molecular dynamics of liquids	nanofluidics
	removal of eddy diffusion	nanochromatography[1]
	enhancement of interfacial thermal conductance	heat dissipation for disruptive microelectronic devices
	magnetic block copolymer	dada storage devices
	solid-like transition (freezing) under electric field	nanofluidics, nanotribology
	enhanced fluorescence signal	sensors
	fluorescence in wide range of wavelength by controlling dye aggregation number	imaging, biological labeling[2]
	melting point depression	adhesion, lubrication, nanotribology
	supercooling of solid–solid transition	adhesion, lubrication, nanotribology
nanoporous solid	high inner surface area, regular pore	gas storage, waste-material treatment, sensor, delivery vehicle, catalysts, carbon dioxide sequestration
	flexible inner surface functionality	removal of toxic metal ions
	selective adsorption and separation of gases	gas chromatography, sensors
	flexible pore size and polydispersity	membrane technology
zeolite	selective diffusion, solid-state acidity	petroleum refining, fine chemical synthesis
	selective diffusion/adsorption	separation technology
metal-organic framework[a]	affinity to hydrogen[a]	hydrogen absorption for fuel cells
	affinity to carbon dioxide[a]	sorbents for gas purification
	high surface area, surface reactivity[a]	catalysts
nano-/micro-porous fiber	selective diffusion/absorption	temperature- and humidity-sensitive fabrics
3-D DNA nanostructure[b,3]	3-D control of DNA functionalities in nanoscale	drug design, nanoelectronics, DNA machines
mesoporous silica	most of the properties of nanoporous solids	most of the applications of nanoporous solids
mesoporous carbon	affinity to hydrogen	hydrogen absorption for fuel cells
	most of the properties of nanoporous solids	most of the applications of nanoporous solids

[a]It depends on the types of organic ligands.
[b]This is the case where the nanopores are created via geometrically matched rational assembly of their building units without the use of template.
[1]Kato et al., 2010.
[2]Spillmann et al., 2009.
[3]Zheng et al., 2009.

TABLE 11-3. Collection of nanoparticle-based nanostructures, their physical and chemical properties that are induced, changed, or enhanced by each nanostructure, and potential applications.

Nanostructure	Property	Potential Application
metal nanoparticle	high catalytic activity	high-yield, low-operating temperature catalysts
	electronic structure tuning	spectroscopic devices, sensors
	melting point depression	catalysts
	band-gap tuning	spectroscopic devices, sensors
	high surface area for functional group	sensors
	unusual interaction with biological cells in both animals and plants	nanotoxicology
	surface plasmon (noble metals)	sensors, medical devices
	fluorescence enhancement (noble metals)	sensors, medical devices
carbon nanotube (single-walled)	sensitive/unusual charge conducting property	real-time NO sensor in biological systems[1]
carbon nanotube	unusual interaction with biological cells in both animals and plants	nanotoxicology
	unusual electronic properties	nanoelectronics
	unusual mechanical properties	nanomechanical devices, stronger/lighter materials
ligand-protected quantum dot (nanoparticle)	magnetic field–, photon-triggered magnetic lineup	spintronics[2]
	quantized double layer charging	charge storage devices
nanostructured electrode	ion and electron transfer	batteries
nanoalignment (of nanoparticles)	tuned/enhanced optical/spectroscopic properties	sensors, energy devices

[1]Kim et al., 2009.
[2]Beaulac et al., 2009.

other intermolecular and colloidal forces) is weak compared with covalent bond, when it comes together along with well-coordinated nanostructural features, it can generate strong and at the same time flexible microscopic and macroscopic forces.

11.6. SUMMARY

There are three basic but intrinsically different nanostructures: nanopore, nanoparticle, and nanofilm. All nanostructures are one of these three. And hierarchical nanostructures are expressed with combinations of any two or three of them. This chapter showed how to design a unique assembly system for each type of nanostructure. It led to the following conclusions:

TABLE 11-4. Collection of nanofilm-based nanostructures, their physical and chemical properties that are induced, changed, or enhanced by each nanostructure, and potential applications. SAM is short for self-assembled monolayer.

Nanostructure	Property	Potential Application
nanocomposite	resistance to crack propagation	materials with enhanced strength/toughness
	improved tensile strength	stronger/lighter materials
	synergistic property combination	multifunctional materials
nanostructured solid surface (usually hierarchical micro-/nano-structure)	superhydrophobicity (lotus leaf effect),[1] superamphiphobicity, superhydrophilicity (superoleophobicity)	medical devices, consumer products, antibioadhesion materials
	wetting transition (Wenzel state ↔ Cassie state): usually by external stimuli	smart materials, microfluidic devices
	friction	coating with controllable friction, lubricants
	adhesion	medical devices, bio-sensors
	frictional adhesion[2]	smart adhesives, moving robots
	size exclusion	surface acoustic devices, gas sensors
graphene	unusual electronic properties	nanoelectronics
nanostructured film: SAM	controlled tuning of surface property	fluidic devices, medical devices, sensors, selective adsorption
semiconductor multilayer	charge generation and transfer	solar cell, lithium secondary battery
conducting polymer multilayer	charge generation and transfer	solar cell, battery
helical composite, biological e.g., collagen, chitosan	unusual functionalities	mimic the functional materials in nature
nanocomposite, biological e.g., nacre, calcite-biopolymer composite	high mechanical strength	mimic the light/durable materials in nature

[1] It is also called super-antiwetting properties. For a comprehensive review, please see Liu et al., 2010.
[2] Zeng et al., 2009.

1. The sizes, shapes, and arrangements of each nanostructure are primarily determined by the sizes, shapes, and arrangements of the self-assembled aggregates.
2. These aggregates should be assembled at the initial step of each assembly.
3. Thus, the design of a proper self-assembly system is the key to nanostructure assemblies.
4. The structural features of each type of nanostructure are defined with a small number of key nanostructural elements.

5. This was the basis for the general nanostructure assembly trends.
6. These in turn help control the nanostructures in a practical manner.

The rational combination of two or three basic nanostructures can provide the possibility of dimensional expansion of nanostructures, which could yield new types of nanostructures and nanoproperties.

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12

Nanoproperties: Controlled to Express

12.1. NANOISSUE

There are two major factors that determine the properties in the nanometer scale (hereafter denoted as *nanoproperty*). The first one is the intrinsic factor and the second one is the structural factor. The nanoproperties that are determined by intrinsic factors are inherited from their macroscale counterparts. The length scales of given materials may belong to the nanometer scale. But their nanoproperties are mainly expressed by the nature of their components, that is, by their macroscale properties. This is an intrinsic factor. When their length scales are decreased, these properties are still independent on the changing length scales for a while, just like bulk materials. However, when the length scales fall into the critical range, which is in many cases somewhere in the nanometer scale, the intrinsic properties are overcome by a structural factor. It is now the sizes that determine the properties of the materials. Thus, it can be stated that nanoproperties from the entire range of the nanometer scale are determined by three different situations. First, they can be solely determined intrinsically even though the sizes are in the nanometer scale. Second, the structural factor can be the sole determinant of the nanoproperties. Third, the nanoproperties can be the result of the combination of the two factors. This is a key facet that makes the expression of nanoproperties unique compared with those from the macroworld, which in turn makes nanotechnology systems unique in general.

Self-Assembly and Nanotechnology Systems: Design, Characterization, and Applications, First Edition. Yoon S. Lee.
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It is inevitable that the issues regarding nanoproperties are directly coupled with the issues regarding nanostructures presented in the previous chapter. This chapter examines the following question:

How can the most effective nanoassembly system be designed for each nanoproperty?

This leads to:

How can nanoassembly building units be selected for a specific nanoproperty?

What are the general rules between the nanoassembly building units?

It is also important to raise the issue of:

What is the general relationship between nanostructures and nanoproperties?

Nanoproperties are classified into three distinctive types in this chapter: individual, collective, and cooperative. The rationale of this classification and the benefits from it are described throughout the chapter. There are many detailed structural factors that can have a significant impact on nanoproperties. These include overall size, the distance between building units, the degree of hybridization between building units, the degree of compositization between building units, the degree of flexibility and rigidity, and so forth. A single structural factor could be the sole reason for a specific nanoproperty. And these could act cooperatively to express another nanoproperty. These issues can be addressed more systematically with this classification.

12.2. GENERAL OVERVIEW

Figure 12-1 is a general overview of the design of a nanoassembly to obtain three different types of nanoproperties (for details on nanoassembly, see Section 2.1). It begins with the distinctive roles of self-assembly and self-assembled aggregates (for the relation of self-assembly with nanoassembly, see Section 2.6), combined with the related overviews from the previous chapters (Figures 2-1, 2-2, 7-1, 8-1, 8-2, and 11-1).

As in the previous chapter, the first step is to identify what type of nanoproperty is necessary for a given purpose. The three types of nanoproperties cover a diverse range of properties including optical, electrochemical, chemical, physical, and mechanical properties. A detailed explanation in relation to nanostructures is described later in this chapter. If the individual type of nanoproperty is the one to be developed, the self-assembled aggregate (*aggregate* for short) that is assembled at the beginning of the assembly should work as *functionalizer* for that nanoproperty. If the nanoproperty is collective, the aggregate should work as *assembler* for the building units involved. If the cooperative type of nanoproperty is to be developed, there should be an aggregate that works as *controller* between the building units.

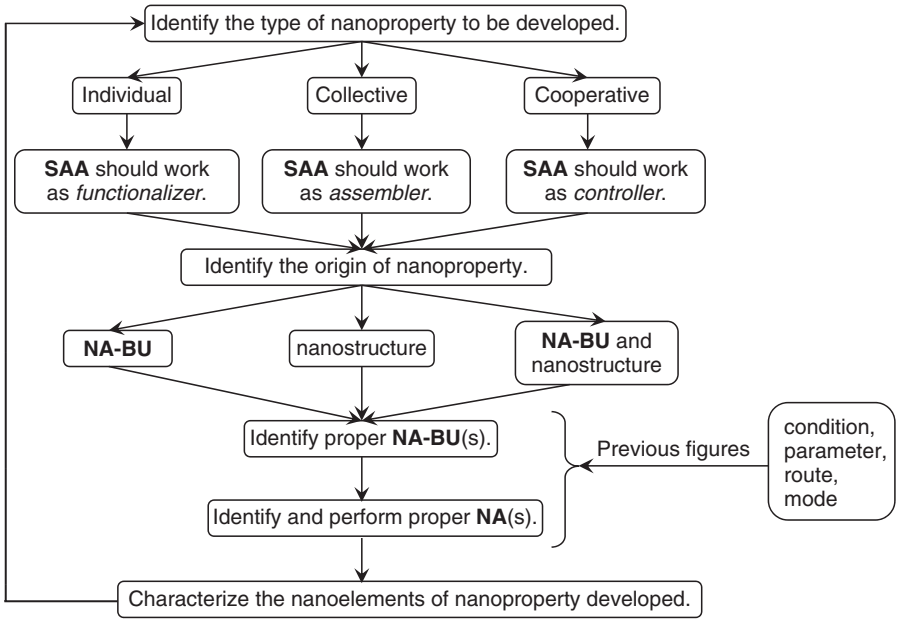


Figure 12-1. General overview of the design of nanoassembly (**NA**) to obtain different types of nanoproperties. **SAA** refers to self-assembled aggregate. **NA-BU** is short for nanoassembly building unit.

Once the type of nanoproperty is determined, its origin has to be identified. As discussed in the previous section, the nanoproperties come from both the nanostructures (structural factor) and the building units (intrinsic factor). Hence, we must identify from which of those factors the nanoproperty to be developed can originate. It can come solely from the building unit, solely from the nanostructure, or from the combination of the two. The building units are selected based on this. The conditions, parameters, routes, and modes of their assembly can be decided by using the overviews in Figures 7-1, 8-1, 8-2, and 11-1. Upon the completion of the assembly, the nanoelements (for their details, see Section 2.3) of each nanoproperty have to be characterized. If they do not satisfy the given purpose, the process should go back to the first step.

12.3. ASSEMBLY PRINCIPLES

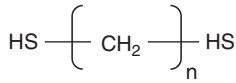
12.3.1. Analysis of Building Units

Figure 12-2 depicts the nanoassembly building units (for details, see Section 2.2) that are used for the assembly to obtain the nanoproperties shown in the chapter. Their segmental structures are also illustrated. As in Figure 11-2, the symbols for each type of building unit come from Figure 2-1; rectangular and circular symbols are used for molecular and colloidal building units, respectively.

(a) **SA-BU:** molecular

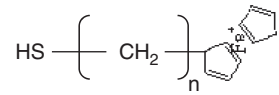
α,ω–alkanedithiol

A D (*conditional*)



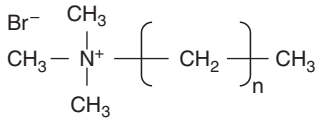
ω-ferroceniumyl alkanethiol

A R EF-F
D (*conditional*)



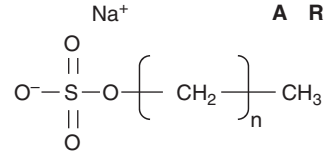
alkyltrimethyl ammonium bromide (ATAB)

A R



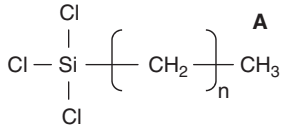
sodium alkyl sulfate (SAS)

A R



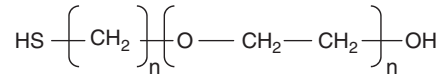
alkyl trichlorosilane

A



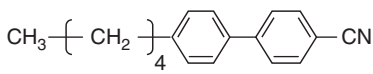
polyethylene oxide chain,
with thiol end group (PEO chain, thiolated)

A R D (*conditional*)



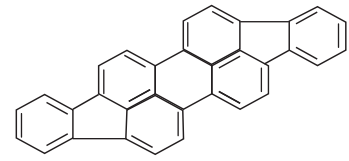
4-cyano-4′-n-pentyl-1,1′-biphenyl (5CB)

A R D



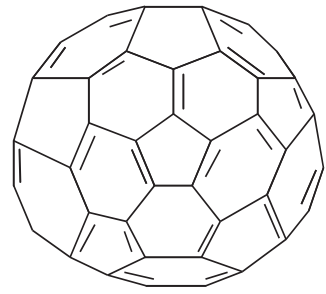
diindenoperylene

A R D



buckminsterfullerene (C_{60})

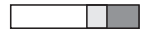
A **R** (*negligible*)



(This a partial structure.)

Figure 12-2. Building units. **SA-BU** and **R-BU** refer to self-assembly and reactive building units, respectively. **A, R, D, AP**, and **EF-F** refer to attractive, repulsive, directional, asymmetric packing, and external force–specific functional segments, respectively.

(b) **SA-BU**: biological ≡

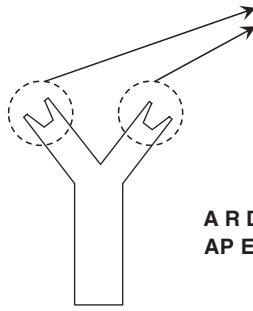


adhesive protein mixture, *lustrin A*-based

A R D AP

antibody: immunoglobulin (Ig)

antigen binding sites



A R D
AP EF-F

(c) **SA-BU:** colloidal

gold (Au) nanoparticle
silver (Ag) nanoparticle
silica (SiO_2) nanoparticle
titania (TiO_2) nanoparticle
cadmium telluride (CdTe) nanoparticle

≡

A R (*negligible*)

silicon (Si) nanorod ≡

A R (*negligible*)

platinum (Pt) nanocube ≡

A R (*negligible*)

(d) **SA-BU**: substrate

indium tin oxide (ITO) surface
glass surface

A R (*negligible*) ≡

gallium arsenide (GaAs) surface
gold (Au) surface

A R (*negligible*) ≡

calcium carbonate ($CaCO_3$) ≡

A R (*negligible*)

silicon (Si) nanogroove ≡

A R (*negligible*)
D (*conditional*)

A R (*negligible*)
D (*conditional*)

silica (SiO_2) nanopore ≡

A R
D (*conditional*)

montmorillonite, layered ≡

Figure 12-2. (*Continued*)

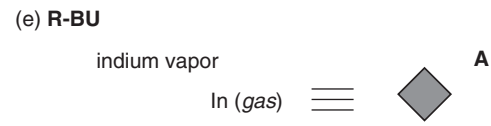


Figure 12-2. (*Continued*)

Figure 12-2(a) has nine molecular self-assembly building units. The last one is fullerene (C_{60}). The shape and size of this particular one is rather close to colloidal particle. However, since it has clear molecular characteristics, it is classified here as a molecular building unit. α,ω-alkanedithiol homologue series have a typical attractive segment that is their hydrocarbon chains as long as the chains are lengthy enough to induce hydrophobic attractive interaction. The two thiol groups at both ends of the hydrocarbon chain could be assigned as a reactive attractive segment. Exactly the same analysis could be applied as for alkylthiol homologue series shown in Figure 11-2(a). However, since these building units have two thiol groups that are located opposite each other, and since in reality the reaction with these groups is very likely simultaneous, they can provide some degree of directional force. This makes them a directional segment, but only conditionally. It will be very obvious, for example, if they are assembled between two narrowly placed gold surfaces.

ω-ferroceniumyl alkanethiol homologue series are the second building unit. Again, as long as they have lengthy enough hydrocarbon chains, they have an attractive segment that induces hydrophobic force. The ferroceniumyl group can be a dual-purpose segment. Its positive charge (as a group, not of iron atom) induces an electrostatic repulsive force whenever the condition is right, which causes this group to be assigned as a repulsive segment. At the same time, it has two planar five-carbon rings connected to each other, and their parallel geometry combined with a ring current effect can drive their position along the direction favored by their geometry. But since this is quite a bulky group, this potential directional force may not be expressed well in most cases. However, it is certain that the ferroceniumyl group is a typical electrochemically sensitive group, which makes it an external force–specific functional segment as well. Figure 9-5 has more details on this type of segmental analysis. The thiol group could become a reactive attractive segment with the same logic as for the thiol groups in α,ω-alkanedithiols. One difference is that it is now located at only one end of the hydrocarbon chain. However, along with the ferroceniumyl group, this single thiol group can also direct its assembly. Hence, it becomes a directional segment as well, but only conditionally.

The third building unit is alkyltrimethylammonium bromide homologue series. It is one of the most typical cationic surfactants with clearly defined attractive and repulsive segments. Figure 11-2(a) has more details on this building unit.

The next one is sodium alkyl sulfate homologue series. They are anionic surfactants. With the hydrocarbon chain lengths of ~8–~18 carbons, they are soluble in aqueous solution, and the hydrocarbon chains provide an attractive hydrophobic force, which makes their attractive segment. The anionic sulfate group is a repulsive segment that induces an electrostatic repulsive force.

Alkyltrichlorosilane homologue series is the next one. Figure 11-2(a) showed the segmental analysis of alkyltriethoxysilanes. The silane-based head groups from these two building units appear to be different. But once they are placed in aqueous solution, the pathway for their reactive interactions is almost the same. They both go through a hydrolysis followed by condensation, which results in the formation of polysiloxanes. Thus, the trichlorosilane group here can also be assigned as a reactive attractive segment. The hydrocarbon chain is their attractive segment.

The next building unit is polyethylene oxide chain with thiol end group. As long as the hydrocarbon chain is long enough, it has no other role but to be an attractive segment. Ethylene oxide group is nonionic. But they induce a hydration repulsive force when they are in aqueous solution. This makes it a repulsive segment. The thiol group is primarily a reactive attractive segment. But this thiol group also can direct the assembly along with the action of repulsive group. It thus makes a conditional directional segment of this building unit as well.

The seventh building unit is a liquid crystal–forming molecule. 4-cyano-4′-*n*-pentyl-1,1′-biphenyl, commonly known as 5CB, has a relatively short pentyl group. But since there is no strong repulsive group within the molecule, this pentyl group seems to be enough to induce an attractive force between them, thus making its attractive segment. The biphenyl group is quite bulky, considering the size of the entire molecule. This is enough to counterbalance the pentyl group as a repulsive segment. It can also direct the assembly through a side-by-side stacking even though the two benzene rings are slightly off-the-plane. This makes this group a directional segment as well. The cyano group at the end of the biphenyl group can provide an additional directional force through hydrogen bonding. Diindenoperylene (also known as periflanthene) is a common dye molecule. The bulkiness of this molecule combined with its multiple benzene rings generates an attractive interaction through van der Waals force along with $\pi-\pi$ interaction. This is its attractive segment. If the dye molecules come close, there will be intrinsic repulsive force also because of this bulkiness. This becomes the repulsive segment of this building unit. The slender molecular shape can cause it to be aligned along the direction of its long axis when it assembles. It thus has a directional segment as well.

The last building unit is buckminsterfullerene (C_{60}). Its attractive segment comes from van der Waals force. Its repulsive segment is negligible, but it can come from possible surface charges during assembly, especially when it is in solution. Thus, it can be conditional, too.

Figure 12-2(b) is for biological self-assembly building units. The first one is a common *lustrin A*–based adhesive protein mixture (Smith et al., 1999). The exact molecular structure and overall morphology of this particular protein mixture are not well characterized even though it is commonly used in various applications. However, based on the fact that this is a protein, it is acceptable that this building unit has attractive, repulsive, and directional segments. Hydrophobic force is the primary source for the attractive segment, which can be reinforced by the directional segment. The areas responsible for the hydrophobic force are located along the protein chains. The same is true for the directional force. Mostly, hydrogen-bond-generating groups make up this directional segment. The repulsive segment is from

the combination of an electrostatic repulsive force with a hydration force. This building unit also can have asymmetric packing segments, possibly in many sites. These segments might already have expressed their asymmetric packing capability during the formation of the higher-order conformation, in other words, during the multi-step assembly to get to the point of the coiled protein morphology.

One difficulty in using this particular protein is whether the expression of asymmetric packing segments would continue when it is introduced into the assemblies to obtain nanoproperties. This, in some cases, can be predicted with a reasonable accuracy, but in other cases it can be determined only retroactively. This uncertainty problem of asymmetric packing segment is a common issue that arises whenever a protein is one of the building units.

The second building unit is an antibody. Antibody is a Y-shaped protein that has huge diversity. Its structure is relatively well characterized. With the same logic as for the adhesive protein mixture, it can be stated that it has attractive, repulsive, and directional segments. The origins for each segment are almost the same as for the adhesive protein mixture. There are asymmetric packing segments, too, but with the same issue of uncertainty. One important difference from the adhesive protein mixture is the antigen binding sites. All antibodies have two antigen binding sites at the end of the two short arms. They are always antigen specific, which means that one particular antibody binds with only one particular antigen. And this binding occurs through a lock-and-key type of structural recognition. Thus, the activation of specific antibody can be viewed as an assembly that is specific on antigenic stimulus. This is not exactly the kind of external signals that were discussed in Chapter 9. But given the fact that the assembly of antibody (antibody–antigen aggregation or complexation) is triggered only by the presence of antigen, it is reasonable to see the two antigen binding sites as its external force–specific functional segment.

Figure 12-2(c) shows colloidal building units. The first five nanoparticles are assumed to be spherical. All of them have an attractive segment, which is van der Waals force. Also, for all of them, it is assumed that there is minimal or no surface charge. This gives them no meaningful repulsive segment. Silicon nanorod is also assumed to have no surface charge. Thus, it has an attractive segment but little or no repulsive segment.

The last building unit is platinum nanocube. It does not have surface charge, either, which means that this nanocube also has an attractive segment but no repulsive segment.

Substrates that become a part of the nanostructures are necessary to expand the scope of the nanoproperties. Figure 12-2(d) shows some representative substrates. All of them are classified as self-assembly building units based on the same logic as in Figure 11-2(c). The symbols for each substrate are denoted differently. Indium tin oxide and glass are denoted by an open rectangle. Gallium arsenide and gold are denoted by a thick filled rectangle. A thin filled rectangle stands for calcium carbonate. All five substrates are assumed to have no surface charge. Thus, they have an attractive segment but no repulsive segment.

The next building unit is a silicon substrate with pre-patterned nanoscale grooves but with no surface charge. It thus has an attractive segment, which is van der Waals

force, and no repulsive segment. This is just like the flat silicon substrate with no surface charge. The nanoscale grooves, however, can guide the assembly when the sizes of the other building units are comparable to the size of this groove. This is done by providing a spatial confinement to the building units. Hence, silicon nanogroove has a directional segment as well, but it is mostly conditional.

The next substrate is silica solid with well-arranged nanopores inside. It has an attractive segment, which is van der Waals force. Its surface charge is assumed to be negligible so that there is no repulsive segment. With the same logic as for silicon nanogroove, when the size and/or morphology of the other building units are comparable to those of the nanopore of this silica, it can guide their assembly. Thus, this substrate also has a conditional directional segment.

The last substrate building unit is montmorillonite. It is one of the typical clays with layered space inside. The compositional nature of montmorillonite can provide plenty of surface charges whenever the condition is right. This gives it a repulsive segment. It also has an attractive segment that is van der Waals force. The layered inner structure of this clay has the nanometer range of regular spacing. As for silicon nanogroove and silica nanopore, this channel type of space can guide the assembly of the other building units with the right sizes and shapes. It thus has a directional segment that is also mostly conditional.

Figure 12-2(e) has one reactive building unit. Indium is another typical element that can be deposited as nanostructures on solid surfaces. As with the germanium and silver vapors shown in Figure 11-2(e), it has an attractive segment only.

12.3.2. Different Types of Nanoproperties

The scope of nanoproperties covers diverse ranges of known and, in many cases, unknown properties. It includes physical, chemical, optical, catalytic, electrochemical, fluidic, and spectroscopic properties, and many more. There can be different ways to classify these diverse aspects of nanoproperties. And the benefits from them could be different. But there is one thing that is always clear. Whenever there is a property that is called a *nanoproperty*, there is a structure that is called a *nanostructure*. This prompts us here to classify the nanoproperties in conjunction with the structural features of the systems that provide the nanoproperties. Nanoproperties are classified as three different types in this section. Each of them has its own distinctive characteristics. But by correlating them with the three different types of nanostructures shown in Chapter 11, they can be explained with one set of structural parameters that are common to all three types of nanostructures. This makes the understanding of the origin and characteristics of the nanoproperties more systematic.

Figure 12-3 gives the definition of three different types of nanoproperties. They are individual, collective, and cooperative nanoproperties. The first step is to define the two key nanostructural parameters. Figure 12-3(a) has this. The three basic types of nanostructures are nanopores, nanoparticles, and nanofilms. For all three, there are two nanostructural parameters whose variations become the key to determine their properties. Depending on assembly system, there can be other nanostructural

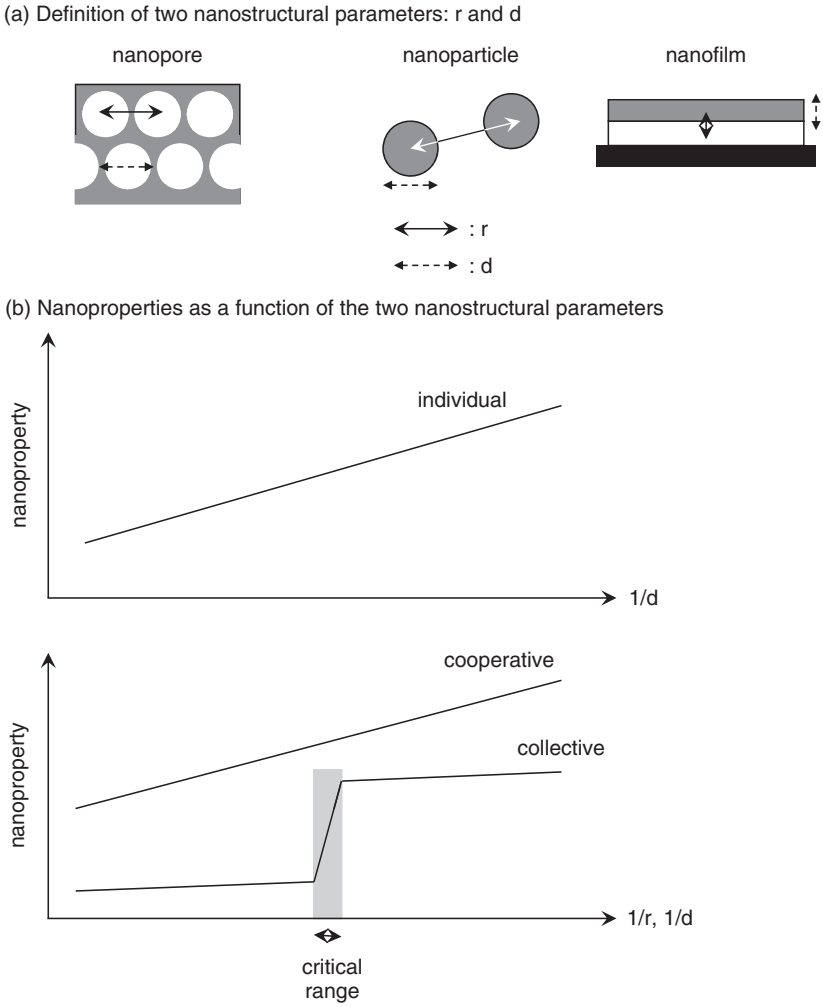


Figure 12-3. Three different types of nanoproperties: individual, collective, and cooperative.

parameters that can affect the expression of a specific nanoproperty. But they are usually specific to each system. The first parameter is the distance between the fundamental units of each nanostructure. This is denoted as r. For nanopore, the fundamental unit is the nanopore itself, thus r for nanopore-based systems is the distance between the two nearest nanopores. For nanoparticle-based systems, this is the distance between the two nearest nanoparticles. And for nanofilm-based systems, it is the distance between the two adjacent layers.

The second parameter is the size of the fundamental units of each nanostructure. This is denoted as d. For nanopore-based systems, it is the size of the nanopore. For

nanoparticle-based systems, it is the particle size. And for nanofilm-based systems, it is the thickness of each layer. Figure 12-3(b) shows the nanoproperties as a function of the two nanostructural parameters. The individual type of nanoproperty is any nanoproperty that is varied linearly as a function of the parameter d. For most systems, the expression of individual types of nanoproperties becomes clearer as the d value is decreased. It does not always have a clear linear tendency, but it is roughly linear with some degree of variation. The effect of the parameter r is minimal or negligible. This nanoproperty is almost independent of the distances, but dependent on the sizes and properties of each building unit. For the collective and cooperative types of nanoproperties, the two parameters are correlated. For the cooperative nanoproperties, their expression is almost linearly increased as primarily the parameter r is decreased. However, it is not uncommon that it is linearly increased as both r and d are decreased; this is the result of the cooperation of the distances and sizes. For the collective nanoproperties, their expression is transitional. There is a critical range of the two parameters. Above the critical values of r and/or d, there is minimal or no nanoproperty expression. This, however, shows an abrupt increase when they reach critical values. The width of this critical range is dependent on each system. Below the critical values of r and/or d, the degree of nanoproperty expression stays high, and usually varies a little as the values of the two parameters keep decreasing.

Case Study 12.1

Studies that show the collective chemical behavior in aggregates of excitable catalyst-loaded colloidal particles (Taylor et al., 2009; Tinsley et al., 2009) can provide some intuitive understanding of the collective nanoproperty. The iron-based particles can trigger an oscillating Belousov-Zhabotinsky (BZ) reaction spontaneously, but only when the aggregates of the particles reach a critical number, which seems to be important to provide a critical distance between the particles so that chemical coupling can occur. The stability of self-assembled dodecanethiol-coated silver nanocrystals against oxygen plasma-induced oxidation (Klecha et al., 2009) provides another reported example of the collective nanoproperty generated by self-assembly. The delicate difference in the distance between the nanocrystals was the key parameter for this stability. For both cases, the critical distances can be viewed as the parameter r in Figure 12-3(a).

The definitions of the three different types of nanoproperties stand valid as long as the structural scale is within the nanometer. Below the nanoscale, which means excessively decreased r and/or d, it goes into the regime of the atomic world, where the interaction is different from the nanoworld. Above the nanoscale, which means excessively increased r and/or d, it goes into the macroworld. Depending on the assembly system, this classification, definition, and variation of nanoproperties can be effective for the macroscale counterparts. However, eventually they will reach the point at which the characteristics of nanoproperties no longer work.

12.3.3. Assemblies to Obtain Nanoproperties

Figure 12-4 presents how self-assembly works for the assemblies to obtain different types of nanoproperties. As mentioned earlier, it works as functionalizer, assembler, and controller to come up with the individual, collective, and cooperative types of nanoproperties, respectively.

For all three assemblies, silver nanoparticle is selected as the starting building unit. The second one is from α,ω-alkanedithiol series. For the first assembly, let 1,10-decanedithiol self-assemble at the surface of silver nanoparticle to form a self-assembled monolayer. For some, both thiol groups might assemble on silver surface. But considering its chain length, for most, only one thiol group assembles on silver surface while the other thiol group is exposed at its outer surface. Then, bring one of the common cantilever tips for the atomic force microscope (AFM). In this figure, silicon nitride (Si_3N_4) is used. Silicon nitride is also well-known to form a self-assembled monolayer with most of the alkanethiols. By properly controlling the condition, it is possible to assemble the remaining thiol groups at the surface of silicon nitride tip. Silver nanoparticle attached on the tip of the atomic force microscope cantilever is useful as a probe for the measurement of colloidal forces. 1,10-decanedithiol functionalized the individual silver nanoparticle, which provides it a new function. It thus is a functionalizer and the resultant nanoproperty is individual. This nanoproperty is solely dependent on the size and property of silver nanoparticle.

The second assembly assembles the aggregates of silver nanoparticles that are regularly interconnected by using the same set of building units. Since the molecular length of 1,10-decanedithiol is fixed, the distance between the silver nanoparticles inside this aggregate becomes constant on average. This is within the range of variation that can be caused by the fluctuation of the hydrocarbon chains such as *cis* or *kink* form. This type of silver aggregates is ideal for spectroscopic substrates including surface-enhanced Raman scattering (SERS). 1,10-decanedithiol does not control the degree of the assembly; it mainly assembles the nanoparticles. It, therefore, worked as an assembler. Not all alkanedithiols from α,ω-alkanedithiol series can work for the assembly of spectroscopic substrates. Depending on the actual system, the average distance between the silver nanoparticles should be at or below the critical value. 1,10-decanedithiol as an assembler provided a collective nanoproperty.

The third assembly in the figure is for the cooperative nanoproperty. The same silver nanoparticle assembles into an aggregate, but this time with alkanedithiols having different hydrocarbon chain lengths. The distance between the silver nanoparticles can be controlled accordingly, which in turn changes the degree of the activity of the silver aggregates. Surface plasmon resonance (SPR) device is one example. α,ω-alkanedithiols worked as a distance controller, and the nanoproperty becomes a function of this distance. It, thus, is a cooperative nanoproperty.

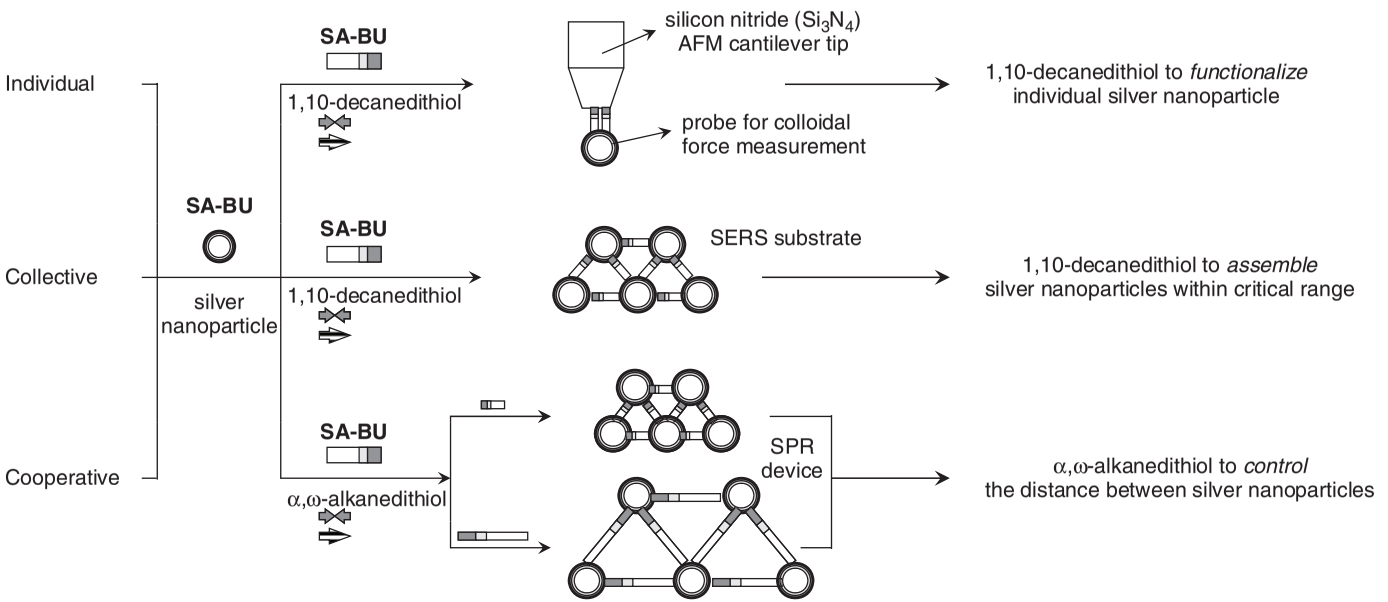


Figure 12-4. General comparison of the roles of self-assembly to obtain different types of nanoproperties. **SA-BU** refers to self-assembly building unit.

12.3.4. Individual Types of Nanoproperties

Figure 12-5 shows assemblies to obtain the individual types of nanoproperties. It has four rounded rectangles that respectively group frame building units, functionalizer building units, nanoproperties developed, and potential applications.

The frame building units are those that express the main nanoproperty. Five building units are selected for this figure. Both their overall morphology and intrinsic property are important for the nanoproperty expression. But it is mainly the size of each building unit that determines each specific nanoproperty. Each frame building unit is functionalized by the second building unit. The functionalizer building units can be any that work to functionalize the frame building units. For all five systems shown here, the attractive or reactive attractive segments primarily drive them to assemble. Repulsive or/and directional segments should be designed properly, whenever they are necessary. The first two systems should be assembled with a certain direction. Surface provides the necessary directionality for the last system. The third and fourth systems do not need a particular directionality.

The nanosystem (for the definition of *nanosystem* and its relation to the nanoscale system and nanotechnology system, see the introductory part of Chapter 2) from the first assembly can have a localized oxidation capability. This nanoproperty is the property that only one side of the nanosystem shows an oxidation activity. Since the oxidation capability is varied as a function of the outer surface area of platinum nanocube, in other words, by the size of the nanoparticle, this is an individual type of nanoproperty. One promising application potential for this nanosystem is a self-propelled nanodevice. If a certain macroscale device is composed of this nanodevice along with others, it becomes a *nanoself-propelled device*.

The second nanosystem produces an electron cascade capability. A stepwise electron flow between two semiconductor nanoparticles through a molecular connector could have great potential for a nanoelectronic device including a field effect transistor (FET) junction. If the length of the functionalizer building unit is fixed, it is the size of the nanoparticle that decides the changes in the electron flow.

For the third nanosystem, cetyltrimethylammonium bromide is placed in solution with the frame building unit, and is allowed to be exchanged with the native metal cations of the frame building unit. This provides an improved ion exchange capability for the clay (montmorillonite). This may find usefulness as an ion exchanger or sorbent. It is the size of the clay, more precisely, the spacing between the layers inside the clay, that changes the ion exchange capability. It thus is an individual nanoproperty. The next nanosystem is assembled with sodium dodecylsulfate and titania nanoparticle. This can generate a unique capability of blocking the ultraviolet light, when it is well dispersed on human skin. Formulation of this nanosystem as an emulsion is the best way to achieve this, and the surfactant building unit is practical to meet this requirement. Hence, sodium dodecylsulfate is a functionalizer. The degree of ultraviolet blocking is almost solely a function of the size of titania nanoparticle, which means that it is an individual nanoproperty.

The last nanosystem is obtained through the assembly of thiolated polyethylene oxide chains on gold surface. By taking advantage of the structural features of gold,

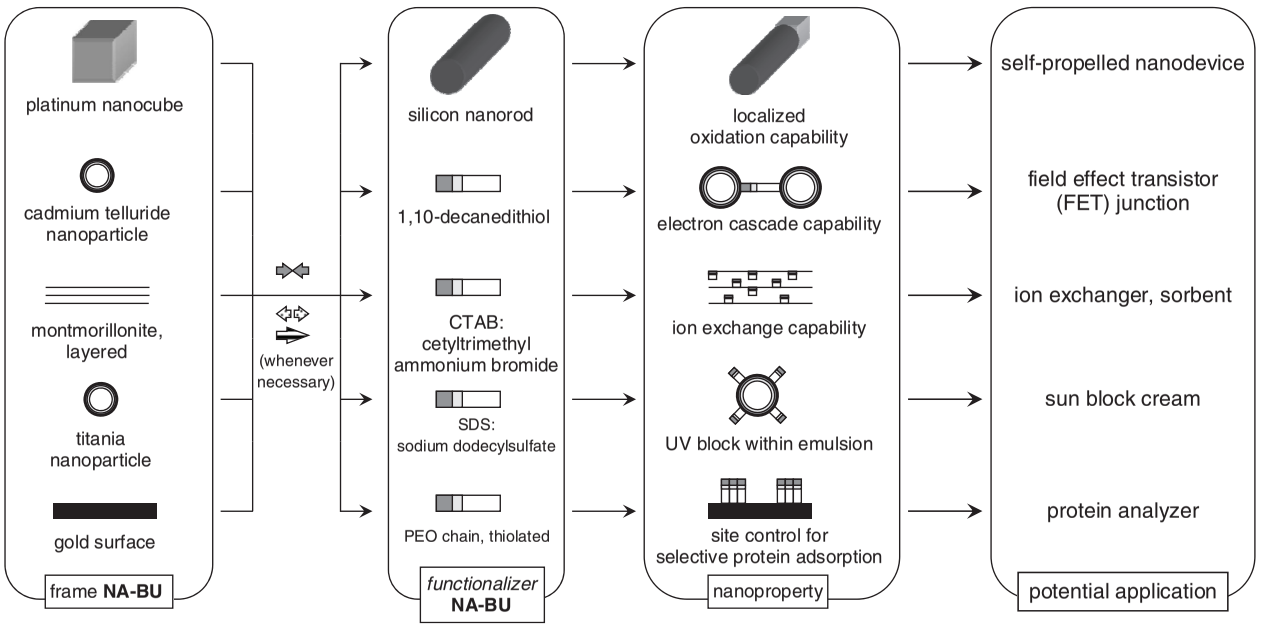


Figure 12-5. Assemblies to obtain the individual types of nanoproperties. **NA-BU** is short for nanoassembly building unit.

the polyethylene oxide chains can be patterned. Polyethylene oxide chain is well-known for its selective adsorption of certain proteins, which can make this system useful as a protein analyzer. The polyethylene building unit is a functionalizer. It is the size of the structural features of gold that primarily determines this capability as an analyzer; thus it is an individual nanoproperty.

Case Study 12.2

Self-assembled cobalt nanoparticle superlattices that display spin-dependent electron transport (Black et al., 2000) may serve as an actual example for an individual type of nanoproperty. The size of the nanoparticles is critical for the proper expression of this property. And the oleic acid monolayers that are assembled on the surface of the nanoparticles provide an insulating organic coating. Oleic acid molecules also play important roles in proving necessary repulsive force that can be balanced with the attractive van der Waals force during the assembly. In terms of the terminology presented here, cobalt nanoparticle is the frame building unit and oleic acid becomes the functionalizer building unit.

Case Study 12.3

Another reported example that is related to the last nanosystem of Figure 12-5 can be found in (Yadavalli et al., 2006). Mixed self-assembled monolayers consisting of *N*-hydroxysuccinimide (NHS)- and hexa(ethylene glycol)-terminated alkylthiols are formed on an ultraflat gold surface. This provides sparsely distributed and exposed NHS groups, which are used to selectively immobilize single proteins on top of the self-assembled monolayers. This nanosystem makes it possible for them to study the unfolding and nanomechanical properties of the proteins in a controlled fashion. The key to this work is obtaining sparsely distributed NHS groups so that the single protein immobilization can be achieved. A structural feature of gold surface (surface roughness to be exact) is the critical parameter for this. Less surface roughness can yield more sparsely distributed NHS groups by avoiding possible highly concentrated NHS groups on rough patches. Hence, this can be viewed as another example of an individual type of nanoproperty. Figure 12-3 defined the individual types of nanoproperties of nanofilms based on film thickness. Surface roughness can be included within this definition of film thickness in the sense that it controls the structural feature of the critical top layer. Thus, the gold surface is the frame building unit for this system since it provides the main nanoproperty (site control). The two alkylthiols functionalize it, which makes them the functionalizer building unit.

Case Study 12.4

An example of an individual type of nanoproperty regarding biomolecules is shown in Gu et al. (2005). This is close to the first nanosystem of Figure 12-4. Silicon atomic force microscope (AFM) tip is modified with tri(ethylene glycol)-based long-chain monolayer, which provides a selective binding site (through

electro-oxidation) for the molecule terminated with a biotin group. This assembly is precise enough to have only one biotin group attached at the tip apex. By working with avidin film, it was possible for them to measure the adhesion force from a single biotin–avidin interaction. The key property for this system is this capability of measuring a single biomolecule interaction, which arises from the biotin-terminated molecule. Thus, the biotin-terminated molecule is the frame building unit here. It was functionalized on the AFM tip by tri(ethylene glycol)-based molecule; hence this molecule becomes the functionalizer building unit. If this frame building unit was a nanoparticle as in Figure 12-4, its property measuring the adhesion force becomes dependent on its size, which is characteristic of an individual type of nanoproperty. However, for this particular system, the frame building unit is a single molecule; that is, this is a case where the parameter d in Figure 12-3 is fixed. But in the sense that (1) no r (another parameter in Figure 12-3) is involved for this system, and (2) even though no effect of d is measured, different d (the size of biotin-terminated molecule) could have affected the force measurement, the capability of measuring a single biotin-avidin interaction here can be considered as an individual type of nanoproperty.

12.3.5. Collective Types of Nanoproperties

Figure 12-6 shows assemblies to obtain the collective types of nanoproperties. The general outline is the same as the previous figure. One difference is that the second rectangle now groups the assembler building units.

There are five frame building units for this figure. The definition of the frame building unit was given in the previous subsection. The first system assembles gold nanoparticles with antibody. Antibody for this particular system has a dual purpose. It first has the driving force that brings the gold nanoparticles together. It assembles at the surface of the gold nanoparticles. These antibody-decorated gold nanoparticles can show a complementarity toward a specific antigen under the right solution assay condition by forming an immune complex. Thus, the antibody is an assembler for this nanosystem, and it is also a part of its nanoproperty because of the antibody–antigen complexation. However, to properly express this antigen complementarity nanoproperty by taking advantage of the gold nanoparticles as a sensing probe, the main structural parameter that has to be controlled is the distance between the gold nanoparticles inside the aggregates. It has to be at the right distance. The role of the size of the gold nanoparticles can be minor. This is a collective nanoproperty. Optical antigen detector could be one possible application. It is intuitive that this antibody–antigen complementarity also takes place through the force balance between their segments. Complexation is achieved at the point, on the profile of their assembly, where all the forces are balanced.

The second system assembles silica nanopore on top of gallium arsenide surface. Silica nanopore also has a dual purpose. To make this type of nanosystem practical in reality, it has to be obtained as a multilayered film. Silica nanopore is usually obtained through a sol-gel process. And it can be designed to assemble the gallium arsenide substrates between the nanopore layers. This makes silica nanopore an

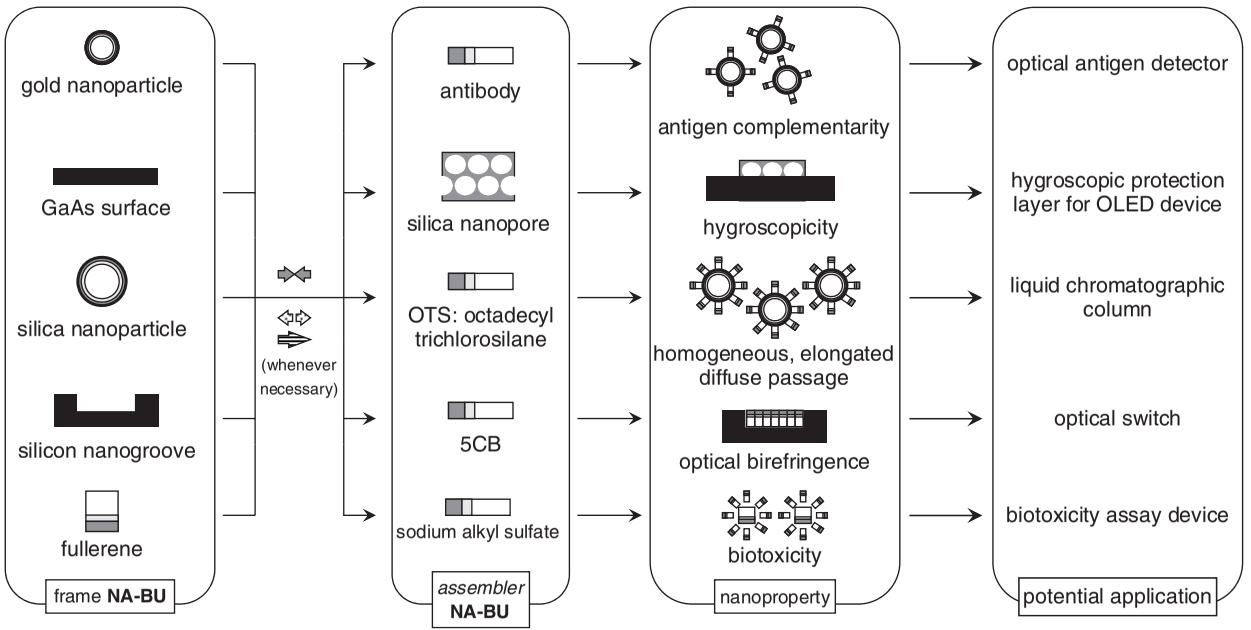


Figure 12-6. Assemblies to obtain the collective types of nanoproperties. **NA-BU** is short for nanoassembly building unit.

assembler building unit. The primary object of this system is to take advantage of the hygroscopic property of silica. Thus, the silica nanopore is also a part of the nanoproperty. The hygroscopicity from the silica nanopore layer, which has a huge inner surface area due to the nanometer pore size, can remove a large amount of water. In addition, it could increase the lifetime of this system substantially by preventing the degradation caused by water. However, it is mainly the distance between the gallium arsenide layers that decides its performance, when it is actually used, for example, for an organic light-emitting diode (OLED) device. The distance should be at or below a certain critical value to maximize its expression. It thus is a collective nanoproperty.

The third system has a liquid chromatography column with the right spacing between the packing materials. The most common chromatography packing material is a silica-based one. This is why silica nanoparticle is selected as a frame building unit. Once this particle assembles with octadecyltrichlorosilanes in solution, its surface is decorated with octadecyl chains through silylation. Then, the surface-decorated silica particles assemble into an aggregate. Octadecyltrichlorosilane is an assembler for this system. To maximize its capability as a chromatography column, this aggregate should have a homogeneous elongated diffuse passage for analytes. And it can be varied by changing the distance between the silica particles. It should be at the right range of distance. It thus is a collective nanoproperty.

The next system builds a base for an optical switch. By directing the assembly of 4-cyano-4′-*n*-pentyl-1,1′-biphenyl (5CB) inside the nanogroove, its molecular orientation can be arranged with a certain direction. The force balance between the attractive and repulsive segments of 5CB that is guided by its own directional segment is the primary driving force for the directionality of this aggregate. The attractive interaction between 5CB and silicon yields 5CB at the silicon surface. Then, it is the directional segment of the silicon that is the nanogroove that makes the 5CB aggregates have a certain pattern and required structural feature. This system can show an optical birefringence property that can be useful for an optical switch type of application. But the maximum expression of the property varies as a function of the length and width of the 5CB aggregates, and the distance between them. These can be determined only by the structural property of the silicon. It thus is a collective nanoproperty. 5CB here surely is an important part of this nanoproperty. But this is not possible without the assembling capability of 5CB inside the nanogroove. 5CB worked as an assembler.

The last system uses fullerene as a frame building unit. It has little difficulty assembling with sodium alkylsulfates once the solution condition is properly adjusted. Instead of assembling them to be two separate aggregates—a fullerene-rich one and a sodium alkylsulfate-rich one—it has to be a form of homogeneous fullerene dispersion whose surface is covered with sodium alkylsulfates. A solution that has a concentration of sodium alkylsulfates above its *cmc* (critical micellar concentration) can more realistically achieve this. The amount of fullerene can be adjusted accordingly so that it can induce a proper attractive interaction with sodium alkylsulfates. This final system could show interesting biotoxicity, which could lead to developing biotoxicity assay devices. Sodium alkylsulfate is clearly

an assembler. The distance between fullerenes, which is mainly determined by the molecular length of sodium alkylsulfates, could be critical for the expression of this biotoxicity assay. It thus is another collective type of nanoproperty.

Case Study 12.5

For more examples of this particular type of nanosystem, please see the reports in Ke and Qiao (2007) and Salonen et al. (2008). These studies include the assemblies of biological molecules on carbon nanomaterials and of surfactant-fullerene systems, and their translocation across biological cell membranes to address the issue of nanotoxicity. Discussions relating to the interactions of the intermolecular forces during the assembly and the translocation can be understood with the concept of force balance. The biological molecules and surfactants are the assembler building units, and the carbon nanomaterials and fullerenes are the frame building units.

Case Study 12.6

Assemblies of microwire-based electrodes from gold (Hermanson et al., 2001) and graphitized carbon (Bezryadin et al., 1999) nanoparticles and their structure–property relationships also are good examples of the collective nanoproperty. For both cases, the metallic electrodes are the frame building units and the nanoparticles are the assembler building units. The electrical properties for both systems show very interesting features, enhanced in some sense compared with those from bulk. This is believed to be the result of the collective charge transport, thereby making them the expression of the collective type of nanoproperty.

Case Study 12.7

Regarding the fullerene-sodium alkylsulfate system, there are studies (Braydich-Stolle et al., 2005; Chen et al., 2007) that provide another good example of the collective nanoproperty. Their systems include fullerenes, carbon nanotubes, and metal nanoparticles. The results clearly show that the nanotoxicity of these nanomaterials is directly dependent on their sizes, shapes, and doses (concentration). The nanotoxicity on biological cells seems to be occasionally reversed at a certain size of the nanoparticles.

Finally, notice that the term *nanodevice* from the previous subsection and the term *device* without the prefix *nano-* in this subsection are different. For the detailed definition of *nanodevice*, see Table 2-3 and Figure 2-9. *Device* in this subsection refers to macroscale devices that have nanoscale components. More details are shown in Chapter 14.

12.3.6. Cooperative Types of Nanoproperties

Figure 12-7 shows assemblies to obtain the cooperative types of nanoproperties. The general outlook is the same as the previous two figures. And the second rectangle now groups the controller building units.

Five solid substrates are used as the frame building units. Figure 12-2(d) showed that all of them had an attractive segment but their repulsive segments were negligible. The definition of the frame building unit was shown in Subsection 12.3.4. Each of the frame building units assembles with five different building units. The first system has diindenoperylene dye building units assembling at the surface of indium tin oxide (ITO). The attractive interaction between diindenoperylene and the substrate attracts them together. Then, the balance between the attractive and repulsive segments of diindenoperylene, which is directed by its own directional segment, aligns it in a certain direction. The substrate provides the two-dimensional overall morphology for this aggregate. Once assembled and aligned on a semiconductor substrate like indium tin oxide, diindenoperylene can show a distinctive charge carrier mobility (or ambipolar transport), which can find an interesting application as an organic nanoelectronic device. Both the thickness of indium tin oxide layer and the distance between indium tin oxide layer and diindenoperylene are critical in order to express this nanoproperty. And it varies almost linearly until it goes out of the boundary. It thus is a cooperative nanoproperty. And the diindenoperylene is the building unit that helps control this nanoproperty through the changes in the assembly degree. Hence, it is a controller of this nanosystem.

The second system assembles calcium carbonate into multilayered composite by using adhesive protein. By taking a layer-by-layer type of successive assembly (for details, see Chapter 7), calcium carbonate and protein can be alternatively layered. The attractive interaction between the protein and calcium carbonate brings them together. Since both this attraction and a certain thickness are necessary for the protein, the repulsive interaction between the repulsive segments of the protein plays a significant role. The structural features generated by the directional and asymmetric packing segments of the protein are expressed within the protein layers. But their importance, in terms of the purpose of this nanosystem, can be ignored. Calcium carbonate–adhesive protein multilayer composite can show a significant improvement in its mechanical properties including fracture resistance. This composite could have a multi-order greater mechanical strength compared with calcium carbonate only. Not only does the adhesive protein improve the flexibility of the substrate, but it works to stop the progression of fracture lines as well. This makes the adhesive protein a controller. The mechanical strength is there as long as the structural features of both layers are within the effective boundary, which means a cooperative nanoproperty. This nanosystem can be a useful basis for the fabrication of ceramic-based devices with a high mechanical strength. The experimental demonstration using the nacre in abalone shell (Smith et al., 1999) explains the underlying principle for this.

The third system assembles ω-ferroceniumyl alkanethiols at gold substrate. The thiol group is reactively attracted at gold surface once they are placed in a proper solution. Then, the force balance between the attractive and repulsive segments of ω-ferroceniumyl alkanethiols assembles them in a certain direction at gold surface. ω-ferroceniumyl alkanethiols have an external force–specific functional segment, which is sensitive on electrochemical signal. Along with the potential role of gold as an electrode, this can make an effective electroactive monolayer that can be

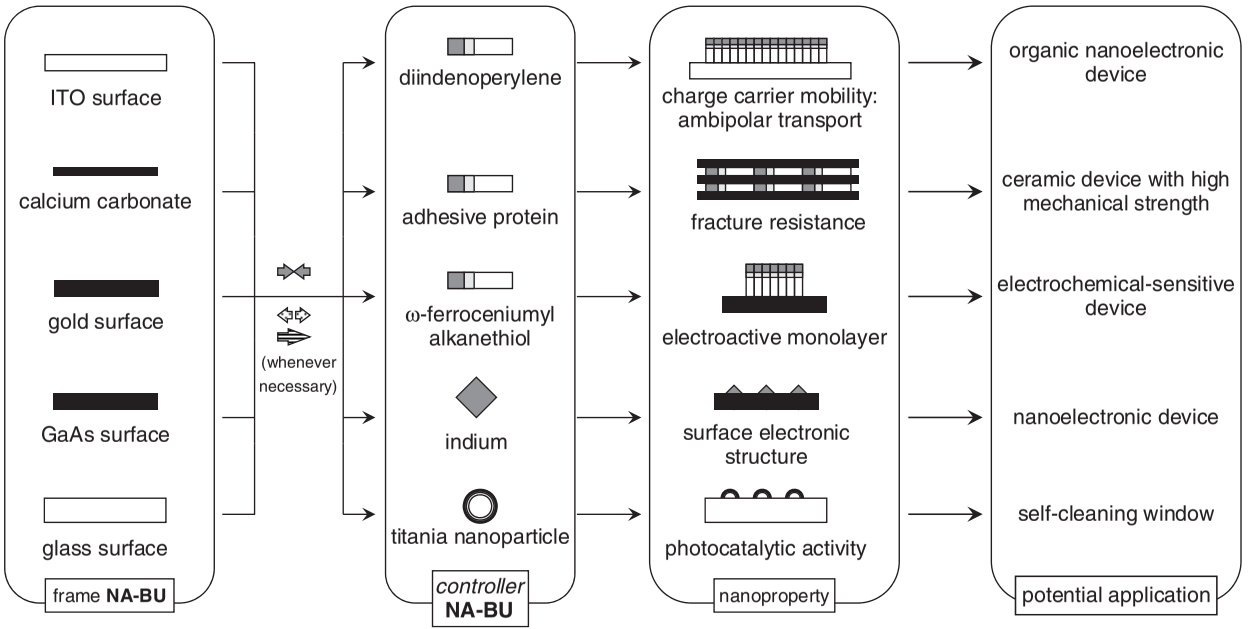


Figure 12-7. Assemblies to obtain the cooperative types of nanoproperties. **NA-BU** is short for nanoassembly building unit.

incorporated into electrochemical-sensitive devices. Structural features including roughness and thickness from both gold and ω-ferroceniumyl alkanethiols are critical for the expression of this property. It thus is a cooperative nanoproperty, and ω-ferroceniumyl alkanethiols are a controller.

The next system assembles indium nanoislands at gallium arsenide substrate. The assembly, in terms of the interaction of their segments, is almost the same as the assembly of germanium islands at silicon surface (Figures 11-6 and 11-8). By controlling the structural features of indium nanoisland, the electronic structure of the nanosystem can be controlled in a systematic manner. This in turn can be applied for nanoelectronic devices. Indium is a controller even though it is a reactive building unit. Structural features from both building units are critical. But their variation is linear as long as they are within a certain boundary. This is a cooperative nanoproperty.

The last system assembles titania nanoparticles at glass substrate. Titania nanoparticle is famous for its strong photocatalytic activity at ambient condition. This particular property is well expressed within the nanometer size range of titania particle, and usually varies linearly as its size changes. In a proper solution, the attractive interaction between glass and titania can be sufficient to assemble titania at glass surface. But in order to have a certain degree of structural order, it might need a forced assembly (for details, see Chapter 8). One of the popular applications for this nanosystem would be a self-cleaning window. Both the size of titania nanoparticles and their number density at glass surface, which is related to the average distance between them, are important for the maximum expression of the photocatalytic activity. And it varies in a linear fashion. For its function as a window, the structural features of the glass are the key. It thus is a cooperative nanoproperty, and titania nanoparticles work as a controller for the property.

For all five nanosystems shown in this subsection, the nanoproperties are acquired by the cooperative coupling of the frame building unit with the controller building unit.

12.3.7. General Trends

Figure 12-8 shows a general trend for the assemblies to obtain three different types of nanoproperties. This is based on the two nanostructural parameters defined in Figure 12-3(a). Generally, as either or both of the parameters are decreased, the nanoproperties are changed from individual to collective and to cooperative. This is not an absolute trend. Their precise changes and the actual nanoproperties can be different depending on each nanosystem. Sometimes they overlap each other. Usually, as the parameters are decreased, the degree of the coupling between building units tends to increase. This also results in the changes in the nanoproperties from individual to collective and to cooperative. Besides the two parameters, the structural complexity and hierarchy of the nanosystem often show a strong correlation with the nanoproperties. Complexity here includes factors such as morphological chirality and the number of building units. The nanoproperties usually show the same changes as the degree of complexity and/or hierarchy of the nanosystem is increased.

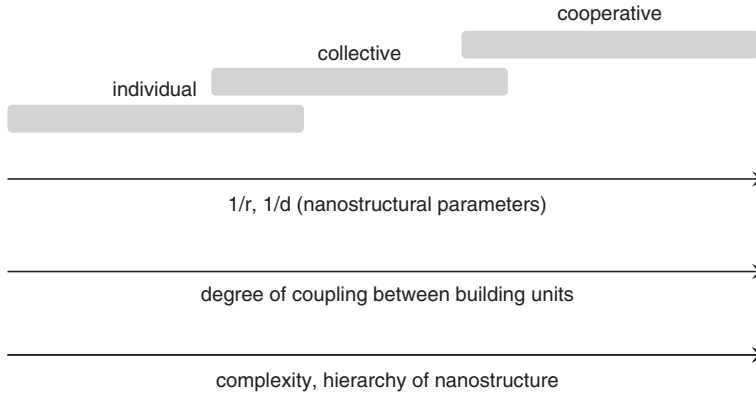


Figure 12-8. General trend of the assemblies to obtain three different types of nanoproperties.

12.4. COLLECTION OF NANOPROPERTIES AND THEIR APPLICATIONS

Tables 12-1, 12-2, and 12-3 show the collection of each type of nanoproperty. Table 12-1 has the individual types of nanoproperties. Table 12-2 has the collective

TABLE 12-1. Collection of the individual types of nanoproperties, nanosystems with which each nanoproperty is expressed, and their potential applications.

Nanoproperty	Nanosystem	Potential Application
functionalization of AFM tips	metal nanoparticles or functional ligands	probe for colloidal or adhesion force measurement
	gold with carbon monoxide-terminated	imaging with atomic resolution (including hydrogen atom)[1]
localized oxidation capability	platinum nanocube	self-propelled nanodevice
electron cascade capability	semiconductor nanoparticles	field effect transistor (FET) junction
ion exchange capability	clays, layered	ion exchanger, sorbents
UV block within emulsion	titania nanoparticle (surface modified with stabilizer and radical scavenger)	sunscreen products
site control for selective protein adsorption	gold surface patterned with thiolated PEO chain	protein analyzer
spin-dependent electron transport	cobalt nanoparticle superlattice	nanoelectronics
transparent conductivity	titania nanoparticle	optoelectronic devices
fast oxidation reaction	aluminum nanoparticle	propellant, jet fuel
micellar solubilization	micelle, vesicle, liposome, emulsion	delivery vehicles, medicines, consumer products
chromo-capillary effect	aggregates of azobenzene-based amphiphiles	photomanipulation of liquid droplets, photoactive materials

[1] Gross et al., 2009.

TABLE 12-2. Collection of the collective types of nanoproperties, nanosystems with which each nanoproperty is expressed, and their potential applications.

Nanoproperty	Nanosystem	Potential Application
spectroscopic property (enhanced Raman intensity)	gold or silver nanoparticle (usually coated with functional shell)	SERS (surface enhanced Raman scattering) substrates
spectroscopic property (surface plasmon resonance)	gold or silver nanoparticle (usually coated with functional ligand)	SPR (surface plasmon resonance) spectroscopy substrates
antigen complementarity	gold nanoparticle modified with antibody	optical antigen detectors
hygroscopicity	semiconductor surface modified with silica nanopore	hygroscopic protection layer for OLED devices
homogeneous, elongated diffuse passage	silica nanoparticle modified with alkyl chains	packing materials for liquid chromatography columns
optical birefringence	semiconductor nanogroove patterned with liquid crystals	optical switches
biotoxicity (nanotoxicity)	fullerene or metal nanoparticles covered with surfactants	biotoxicity assay devices
Belousov-Zhabotinsky reaction	catalyst-loaded colloidal particles	soft smart materials
stability against oxidation	metal nanoparticles coated with SAMs	devices and substrates with enhanced stability
collective charge transport	microwire-based electrodes	nanoelectronics
antimicrobial activity	silver nanoparticle (surface covered with cationic charge)	antiviral agents, building materials, consumer products,
bactericidal activity	titania (anatase) nanoparticle under near UV light, diamond-like carbon, zinc oxide nanoarray	biomedical device coating
quasicrystalline order	nanoparticle (binary) superlattice[1]	nanoelectronics, optics, catalysts

[1]Talapin et al., 2009.

types of nanoproperties. And Table 12-3 has the cooperative types of nanoproperties. As with the collection of nanostructures shown in Section 11-5, these are the ones that appear frequently in the literature, but this is certainly not a complete collection. Nanosystems that express each nanoproperty are shown in the second column. These are the most often studied ones, and not the only ones for each nanoproperty. Potential applications in the third column are those that have a strong potential for each nanoproperty, and some of them are already in use.

12.5. SUMMARY

There are three basic but distinctively different nanoproperties. These are the individual, collective, and cooperative types of nanoproperties. This chapter showed

TABLE 12-3. Collection of the cooperative types of nanoproperties, nanosystems with which each nanoproperty is expressed, and their potential applications.

Nanoproperty	Nanosystem	Potential Application
spectroscopic properties	metal nanoparticles	spectroscopic substrates
surface plasmon resonance	ligand-protected noble metal nanoparticles	optical devices, sensors, medical devices
charge carrier mobility: ambipolar transport	ITO surface covered with diindenoperylene layers	organic nanoelectronic devices
fracture resistance	calcium carbonate multilayered with adhesive protein	ceramic devices with high mechanical strength
electroactive monolayer	gold surface modified with ω-ferroceniumyl alkanethiol layers	electrochemical-sensitive devices
surface electronic structure	GaAs surface patterned with indium nanoislands	nanoelectronic devices
photocatalytic activity	glass surface modified/patterned with titania nanoparticles	self-cleaning window
photocatalytic activity	titania nanoparticle	water purification, medical devices, cleaning devices
photoelectric response	metal or metal oxide nanoparticles assembled with dyes	waveguide devices, sensors, optoelectronics
photochemical response	self-assembled dye nanostructures	artificial photosynthesis, optoelectronics
photochromic effect	diarylethene monolayer on semiconductor surfaces	photoswitching for molecular electronic devices

how to design assembly systems to obtain each type of nanoproperty. It further showed that:

1. The types of nanoproperties are primarily determined by the different roles of self-assembly.
2. These roles should be defined at the initial step of each assembly.
3. Thus, the design of a proper self-assembly system is a key for the assemblies to obtain nanoproperties.
4. The relationship between nanostructures and nanoproperties is inheritable, that is, when there is a structural change, there is a property change.
5. Most of the variations in nanoproperties can be explained using the two basic nanostructural parameters.
6. This was the basis for the general assembly trends of nanoproperties.
7. These in turn can help control the nanoproperties.

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13

Nanofabricated Systems: Combined to Function

13.1. NANOISSUE

To use nanotechnology systems in reality, they have to be fabricated properly. This is done not only by using assembly building units, but in many cases by including bulk materials as well. Semiconductor substrates are a good example. For the nanotechnology systems shown in the previous four chapters, the assembly principles were primarily based either on thermodynamic, kinetic, or manipulative processes. However, since the sizes of most of the bulk materials are at or above the macroscale, an additional process is necessary. This is where the mechanical process comes into play. Generally, the term *assembly* is used when there are no mechanical processes involved. The term *fabrication* is used when mechanical processes are involved. And when the fabrication takes place within the nanoscale, the term *nanofabrication* is widely used. Table 2-3 and Figure 2-9 showed some details of nanofabrication. They also presented details of nanofabricated systems and nanointegrated systems, and the relation of nanofabrication to self-assembly and nanoassembly. Nanofabrication expands the nanoassembly (for details, see Section 2.1) further into the macroworld so that it can make nontraditional building units available for nanotechnology systems. There are three main approaches to nanofabrication: bottom-up, top-down, and bottom-up/top-down hybrid approaches. The bottom-up approach is to build up nanotechnology systems using only assembly building units. The top-down approach, on the other hand, carves out the bulk materials until the nanotechnology systems are obtained. And the hybrid approach

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uses both approaches during fabrication. This chapter looks at the following questions:

How can the most effective nanofabrication be designed for each nanofabricated system?

How can the building units and top-down techniques be chosen for a specific nanofabricated system?

How do the building units interact with each other and with the instruments during top-down processes?

Nanofabricated systems inevitably correlate with nanostructures and nanoproperties. Other issues include the flexibility and comparability of assembly building units with top-down techniques. To have a successful nanofabrication, top-down techniques should be applicable not only over a wide range of length scales, but across different assembly processes as well. The ultimate goal of nanofabrication is the mass production of nanotechnology systems with satisfactory controllability and precision. This aspect will be also discussed in this chapter and the next.

13.2. GENERAL OVERVIEW

Figure 13-1 is a general overview of the design of nanofabrication to obtain nanofabricated systems. Details on assembly conditions, parameters, routes, and modes are shown in Figures 7-1, 8-1, 8-2, and 11-1. The detailed relationships of nanodevices and nanomachines to nanofabricated and nanointegrated systems will be shown in the next chapter.

The first step is to identify the nature of the nanofabricated and/or nanointegrated systems to be developed. Then, the main approach should be indentified from among the bottom-up, bottom-up/top-down hybrid, or top-down approaches. The overall size of the nanofabricated system can be a first-hand guide. And the nature of the components, including the nanostructures that are required to be built and the nanoproperties that should be expressed, can serve as good indicators of whether nanofabrication would be possible through a pure assembly process or whether the intervention of top-down techniques might bring a better outcome. If it appears that the best possible nanofabrication is the bottom-up approach, it should be followed by the selection of assembly building units. The bottom-up approach does not necessarily mean that there should be no usage of top-down techniques. It means that the nanofabrication is purely achieved through the assembly of the building units. It would be ideal if this could be done without top-down techniques. However, as long as those techniques are used to promote more effective assembly of the building units without any mechanical process, it is considered as a bottom-up approach. If the hybrid approach is selected, it means selecting the building units and proper top-down techniques. These techniques should be comparable to the building units selected. If the top-down approach is selected, it is the starting bulk materials that should be selected next. Assembly building units are not necessary for this approach. An important decision to make is which top-down techniques should be used.

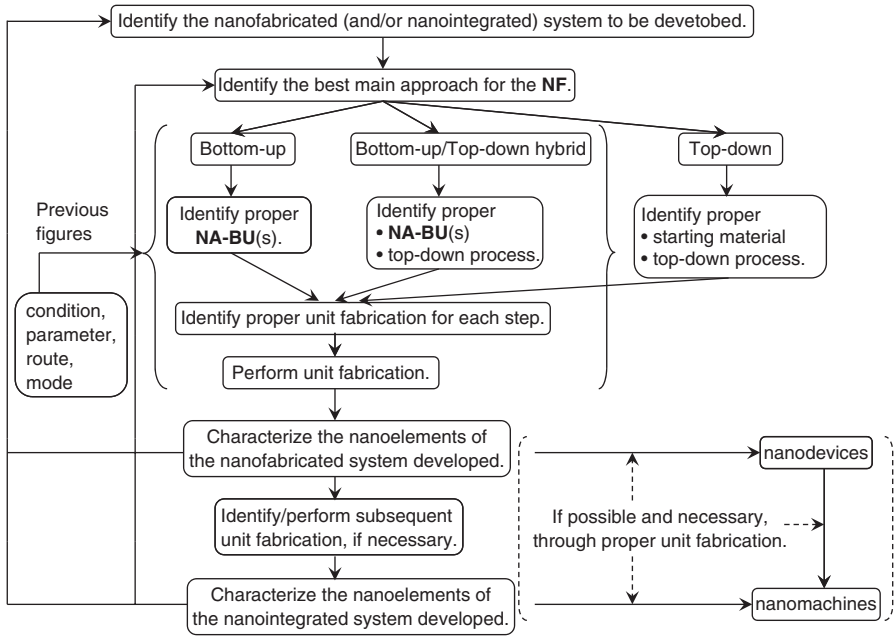

Identify the nanofabricated (and/or nanointegrated) system to be devetobed.
Identify the best main approach for the NF.
Bottom-up
Bottom-up/Top-down hybrid
Top-down
Previous figures
Identify proper NA-BU(s).
Identify proper • NA-BU(s) • top-down process.
Identify proper • starting material • top-down process.
condition, parameter, route, mode
Identify proper unit fabrication for each step.
Perform unit fabrication.
Characterize the nanoelements of the nanofabricated system developed.
nanodevices
Identify/perform subsequent unit fabrication, if necessary.
If possible and necessary, through proper unit fabrication.
Characterize the nanoelements of the nanointegrated system developed.
nanomachines

Figure 13-1. General overview of the design of nanofabricated systems. **NF** and **NA-BU** are short for nanofabrication and nanoassembly building unit.

Regardless of the approach taken, the next step is to perform the nanofabrication. It can be a single-step or multi-step process. The same principles of all-at-once, successive, sequential, or hierarchical assembly modes from Chapter 7 are applied at each step of the nanofabrication. The principles of spontaneous or forced assembly routes from Chapter 8 can be applied to help make the nanofabrication more effective. The detailed nanofabrication processes were classified into 12 unit fabrications (Lee, 2008). All nanofabrication processes belong to either one unit fabrication or a combination of two or more unit fabrications. The result is the nanofabricated system. Its nanoelements (for details, see Section 2.3) should be characterized next. If they do not satisfy the given purpose, the process should go back to the first step, either to adjust the nanofabricated system or to change the main approach for it. The nanointegrated system is obtained when this nanofabricated system is fabricated further through unit fabrications.

13.3. FABRICATION PRINCIPLES

Nanofabrication includes self-assembly and nanoassembly (for details on the relationships among self-assembly, nanoassembly, and nanofabrication, see Section 2.6). The title of this section comes from this definition. The top-down techniques here indicate all the instruments or mechanical processes that are used for nanofabrication.

13.3.1. Analysis of Building Units

Figure 13-2 shows the nanoassembly building units (for details, see Section 2.2) that are used for the fabrication of nanofabricated systems shown in this chapter. Their segmental structures are also shown. As in Figure 12-2, the symbols for each type of building units come from Figure 2-1, and rectangular and circular symbols

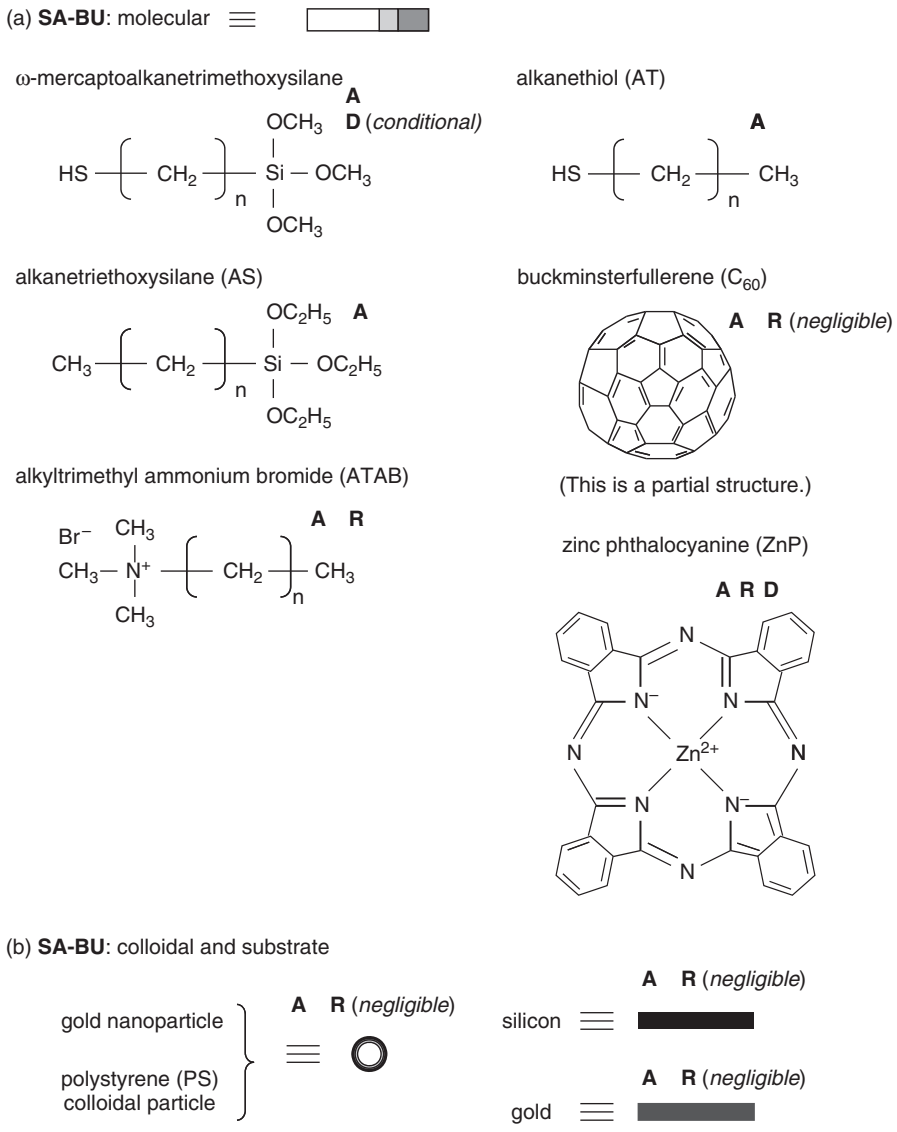
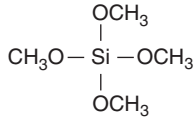


Figure 13-2. Building units, starting bulk materials, and top-down techniques. **SA-BU** and **R-BU** refer to self-assembly and reactive building units, respectively. **A, R**, and **D**, refer to attractive, repulsive, and directional segments, respectively.

(c) **R-BU**

tetramethylorthosilicate (TMOS)



silver vapor

Ag (*gas*)

≡ **A**

(d) Starting bulk materials

- gold
- copper
- silicon
- polydimethylsiloxane (PDMS)
- silicon carbide
- indium tin oxide (ITO) glass

≡

(e) Top-down techniques

- atomic force microscope (AFM)
- scanning tunneling microscope (STM)
- optical tweezers (OT)
- mechanical grinder, sieve (mesh)
- photolithography

(f) Metal-organic framework (MOF)

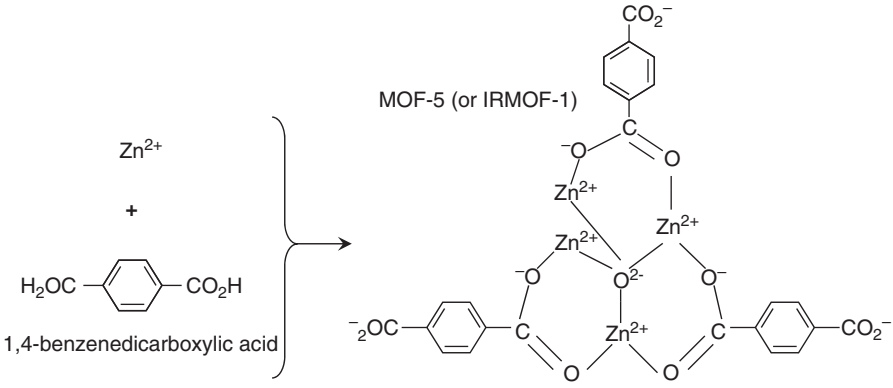


Figure 13-2. (*Continued*)

are used for molecular and colloidal building units, respectively. It also shows the bulk materials that are used for top-down methods, and some typical top-down techniques.

Figure 13-2(a) has molecular self-assembly building units. ω-mercaptoalkane trimethoxysilane homologue series have a well-defined attractive segment. As long as the hydrocarbon chains are long enough, they induce an attractive hydrophobic force. They have a thiol group at the end of the hydrocarbon chain, and trimethoxysilane group at the other end. Since both of them are reactive, they become a reactive attractive segment. Building units with similar segmental structure, α,ω-alkanedithiol homologue series, were analyzed in Figure 12-2(a). They also had two reactive attractive segments at both ends of the hydrocarbon chain. But the difference is that the two reactive groups were the same in α,ω-alkanedithiols while they are different in ω-mercaptoalkane trimethoxysilanes. This difference certainly generates a different degree of attractive symmetry when they induce a directional force. For example, almost the same degree of thiol–gold interaction can be expected when α,ω-alkanedithiols meet with a gold surface. For ω-mercaptoalkane trimethoxysilanes, a directional force can be induced either in a separate way or as the dual-type. If they meet with gold or silica surface, the thiol or silane group reactively interacts with the gold or silica, respectively. If the gold and silica happen to be at the right distance with ω-mercaptoalkane trimethoxysilanes in between, both reactive groups are attracted onto the gold (thiol group) and silica (silane group). This will direct the assembly of the whole system. It thus is obvious that both thiol and silane groups are a directional segment. But they have to be at the right condition to express this capability. This is the logic that, as with α,ω-alkanedithiols, the two reactive groups in ω-mercaptoalkane trimethoxysilanes are assigned as a conditional directional segment.

Alkanethiols and alkanetriethoxysilanes were analyzed in Figure 11-2(a). Both have a long hydrocarbon chain, which is their attractive segment. They also have a reactive attractive segment that can reinforce the attractive segment. For alkanethiols, this is the thiol group, while it is the silane group for alkanetriethoxysilanes.

The next building unit, fullerene, was shown in Figure 12-2(a). It has an attractive segment, and its repulsive segment is negligible. The reason why fullerene is viewed as a molecular building unit was discussed in the same figure. Alkyltrimethylammonium bromide homologue series are a typical cationic surfactant. They have both attractive and repulsive segments as shown in Figure 12-2(a). One of the typical photoactive molecules, zinc phthalocyanine, is the next unit. A dye molecule, diindenoperylene, as shown in Figure 12-2(a) had attractive, repulsive, and directional segments. With similar logic, zinc phthalocyanine is also assigned to have all three segments. Much of their origin is in its multi-ring system. The zinc ion at the center can provide an additional directional force via coordination bonding.

Figure 13-2(b) has colloidal building units and substrates. Assuming the same condition as for the gold nanoparticle in Figure 12-2(c), the gold nanoparticle here has an attractive segment, and its repulsive segment is negligible. The same goes for polystyrene colloidal particle. As with the polystyrene colloidal particle

in Figure 11-2(b) that had minimal surface charge, the polystyrene particle here is assigned to have an attractive segment with a negligible repulsive segment. The two substrates (silicon and gold) also have an attractive segment with a negligible repulsive segment. This is based on the same assumption for the silicon and gold surfaces in Figures 11-2(c) and 12.2(d), respectively.

Figure 13-2(c) is for reactive building units. Tetramethylorthosilicate is another common precursor, as with tetraethylorthosilicate, that is widely used for fabrication of silica-based nanostructures through the sol-gel process. They have very similar molecular structure and their hydrolysis–condensation processes are almost the same in aqueous solution. This gives them the same segmental analysis. As shown in Figure 11-2(e), tetraethylorthosilicate has only an attractive segment. The same goes for tetramethylorthosilicate. Silver has only an attractive segment, too, as shown in Figure 11-2(e).

Figure 13-2(d) shows the bulk materials that are used for top-down methods. The range of sizes and morphologies that define the term *bulk* is not definitive. These are the materials that can be carved out by mechanical processes to come up with nanostructures. Hence, as long as they meet with this criterion and as long as the subsequent physical and chemical properties do not adversely affect the processes, they can be viewed as the starting bulk materials for nanofabrication, no matter what their actual sizes and morphologies might be. But the critical difference from the substrates is that, for the bulk materials, the whole material is under nanofabrication, while only the surface is under nanofabrication for the substrates.

Figure 13-2(e) shows some of the widely used top-down techniques. The atomic force microscope (AFM) and scanning tunneling microscope (STM) are popular because of their capability for precision manipulation of a variety of building units on solid surfaces. Optical tweezers can make this manipulation possible beyond the surface. A mechanical grinder is a simple apparatus that can perform the particle size sieving. Lithographic techniques such as photolithography become useful when mass production of a certain fixed nanopattern is necessary on solid surfaces. A variety of photoresists for this technique are commercially available, including PR5214, AZ-P 4620, Microposit series, and SU-8.

Figure 13-2(f) shows the synthesis of a metal-organic framework. This is not for a segmental analysis of the building units. Rather, it is to show that the concept of force balance becomes useful often beyond nanofabricated systems. This material is synthesized through strong coordination bonding. Unlike the typical assemblies that were discussed in the previous four chapters, no interactions are driven by intermolecular or colloidal forces here. When one of the building units, zinc cation, is stoichiometrically mixed with the second building unit, 1,4-benzenedicarboxylic acid, they form a well-arranged unit structure of zinc-benzenedicarboxylic acid complex. This unit structure grows directionally and forms a well-developed network. The formation of unit structure complex is spatially determined by the structural characteristics of benzenedicarboxylic acid. This can be viewed as a repulsive act (steric) that counterbalances the attraction, which is the bonding of zinc cation with oxygen atoms. The complex is formed when these two interactions

are balanced. And the result of the spatial balance happens to be the best condition that gives a unique void space inside of it. This inside space is thus almost monodisperse, and its size becomes a few nanometers. This is why it is also called nanoporous metal-organic framework.

Shown in Figure 13-2(f) is a typical metal-organic framework, called MOF-5 or IRMOF-1. Thanks to their easy synthesis, and to the wide availability of metal ions and organic ligands, numbers and types of newly discovered metal-organic frameworks keep growing rapidly (Mueller et al., 2008; Rowsell and Yaghi, 2004) (for a comprehensive listing of them, see Table 7-4). More about their physical and morphological properties, especially compared with a similar family of materials, mesoporous silicas, is discussed in Case Study 13.3 in Subsection 13.3.5.

13.3.2. Nanofabrication

Figure 13-3 shows a general comparison among the three main approaches to nanofabrication. For clarity, the same silicon substrate is used for all three approaches. First, for the bottom-up approach, 12-mercapto dodecanetrimethoxysilane and 1-decanetrimethoxysilane assemble on the silicon surface. Both building units have the same silane reactive attractive segment. This readily undergoes hydrolysis followed by silylation with silicon. By carefully managing the surface phase separations on the silicon surface, it is possible to have their self-assembled monolayer in a patterned form. The silicon surface provides a directional force. The areas where 12-mercapto dodecanetrimethoxysilane is located have greater thickness (the length of two carbon–carbon bonds) than those of 1-decanetrimethoxysilane. The tops of these areas are functionalized with thiol groups. Now, by carefully introducing gold nanoparticles, the thiol groups can be selectively attached to them through thiolation. This is a jointing unit fabrication (Lee, 2008). The areas where 1-decanetrimethoxysilane is located work to buffer the gold nanoparticles between them. This is a nanofabricated system of patterned gold nanoparticles fabricated with four different building units. It is performed purely via nanoassembly without any intervention of mechanical process. Therefore, it is a bottom-up approach.

For the hybrid approach, only 12-mercapto dodecanetrimethoxysilane assembles on the surface of silicon. Through almost the same process as for the bottom-up approach, it forms a well-developed self-assembled monolayer. But unlike the above mixed self-assembled monolayer, its entire upmost layer is covered with thiol groups. There is no pattern formed at this step. The atomic force microscope (AFM) can manipulate solid surfaces with nanometer resolution. By mechanically scratching this self-assembled monolayer with the AFM tip, it can be patterned with sizes and structures controlled by us. And by performing jointing unit fabrication with gold nanoparticles, a nanofabricated system whose surface is patterned with gold nanoparticles is fabricated. Three different building units are used, which is one fewer than the previous bottom-up approach. However, to obtain the right pattern, the top-down technique had to be used. The bottom-up approach is combined with the top-down approach.

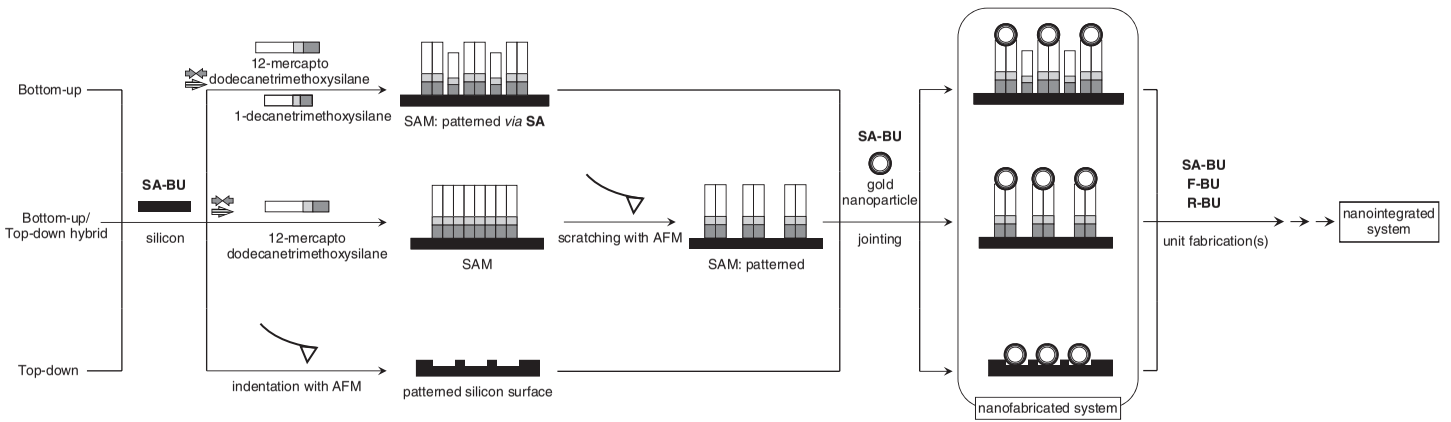


Figure 13-3. General comparison of the three main approaches to nanofabrication. **SA-BU, F-BU**, and **R-BU** refer to self-assembly, fabrication, and reactive building units, respectively. **SA** and SAM are short for self-assembly and self-assembled monolayer, respectively.

For the top-down approach, the silicon surface is first patterned with AFM through indentation. Indentation using AFM can offer up to the nanometer range of resolution. This patterned silicon then undergoes jointing unit fabrication with gold nanoparticles. The gold nanoparticles can be placed only on the patterned area, for example, by gently shaking them or by gliding them with a proper slope. No bottom-up assembly is necessary. The entire fabrication was through mechanical process. Thus, it is a top-down approach. It needed only two building units. A direct indentation on a hard surface like silicon can provide more operational freedom than the scratching, which could help generate patterns with delicate controllability. However, it usually comes at the price of a long, time-consuming process and heavy labor.

Nanofabricated systems can be fabricated further into nanointegrated systems. Two or more nanofabricated systems can be fabricated through unit fabrications. Depending on the system, this fabrication can be performed with or without additional building units. Additional bulk materials, whenever the top-down approach is involved, can be used. For both nanofabricated and nanointegrated systems, their characterization should cover all four nanoelements (for details, see Section 2.3). It should be a common practice to characterize their nanostructural and nanoproperty elements to confirm the intended nanostructures and nanoproperties, and to correlate them together, which is critical for their actual applications. In addition, it is important to realize that many nanofabricated and nanointegrated systems are actually nanodevices and nanomachines. This is especially the case for many nanointegrated systems. It thus is necessary to properly characterize nanomechanical and nanocommunication elements to check whether this indeed is the case.

Each of the three approaches has its advantages and disadvantages. Depending on the nature of the fabrication system and the uniqueness of its building units, the practicality of each approach can be widely different. Only one specific approach could be useful for a specific nanofabricated system, or all three could be practical for another system. There is a study by Genzer and Bhat (2008) that reviews the fabrication of surface-bound gradient structures on soft materials, which further leads to the development of functional surfaces and materials. This article provides good examples that can be compared in parallel with the examples shown in this figure.

13.3.3. Bottom-Up Approach

Figure 13-4 shows how the bottom-up approach works for nanofabrication. The bottom-up approach is defined as any type of fabrication that fabricates nanofabricated systems using only assembly building units. This does not mean that top-down techniques are not involved at all. As long as top-down techniques are there to help achieve a proper assembly of the building units, and as long as they do not carve out any part of the building units, it is still considered as a bottom-up approach. The use of top-down techniques in this sense can be viewed as a part of forced or directed assembly.

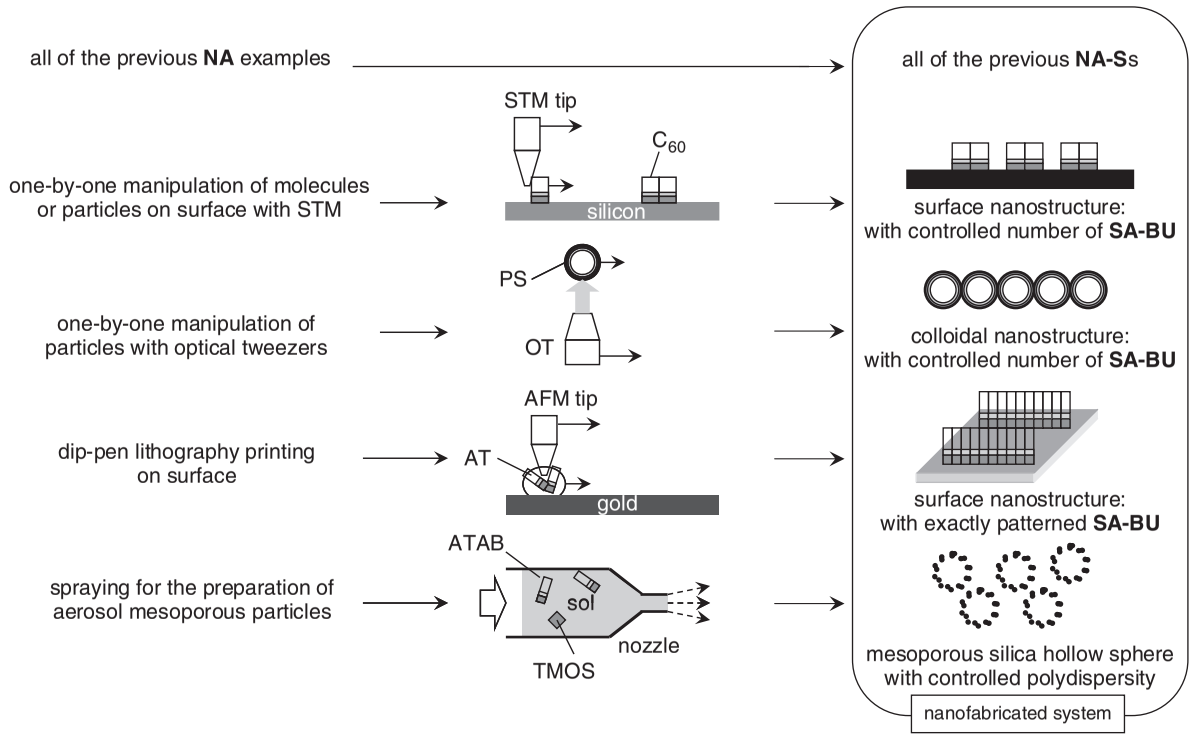


Figure 13-4. Bottom-up approach to nanofabrication. **SA-BU** refers to self-assembly building unit. **NA** and **NA-S** are short for nanoassembly and nanoassembled system, respectively.

Nanofabricated systems include nanoassembled systems (for details, see Figure 2-9), and nanoassembled systems are obtained through nanoassembly. This suggests that all of the assemblies that were shown in the previous chapters (Chapters 7, 8, 9, 10, 11, and 12) are bottom-up nanofabrications. The second system assembles individual fullerene building units on the surface of silicon substrate. Careful use of the scanning tunneling microscope (STM) can make one-by-one manipulation of fullerenes possible. By moving individual fullerenes with an STM tip through the repetition of contacting, pushing, and leaving operations, it is possible to assemble fullerenes on a specific location. Shown in Figure 13-4 is the surface nanostructure that can be obtained with a controlled number of fullerenes. There is a study by Dietzel et al. (2009) that demonstrates the one-by-one manipulation of antimony nanoparticles on the surface of highly oriented pyrolytic graphite (HOPG) with the tip-on-top approach. Their discussion about the underlying microscopic mechanism based on the friction forces is very intuitive.

Case Study 13.1

When performing one-by-one manipulation, the most difficult hurdle is not how to contact-and-push (or grasp-and-move) an object but how to leave (release) the object at a desired position. Attractive intermolecular/colloidal forces allow us to catch and move the object, but they become a problem when releasing it. There is an excellent work by Dejeu et al. (2009) that clearly demonstrates the power of self-assembly principles to solve this important issue. They first rationally modified the surface of the tip or the glass colloidal particle with a self-assembled monolayer of aminosilanes. By simply changing the solution pH, they were able to control the surface charges, thus switching the interaction between the tip and particle from attractive (during grasping and moving) to repulsive (during releasing).

The third system manipulates polystyrene colloidal particles in two- or three-dimensional space. A careful one-by-one assembly with optical tweezers can make this possible. The outcome is the colloidal nanostructure with a controlled number of polystyrene building units. For details on apparatus setup and experimental conditions, and a discussion regarding the interaction among the forces involved, see Stout (2001). The strength of the forces generated by optical tweezers is within the range of picoNewton, which is comparable to the intermolecular and colloidal forces.

Case Study 13.2

Another report (Ognysta et al., 2009) further demonstrates the practicality and precision of one-by-one assembly of colloidal particles using optical tweezers. What is more interesting from this study is that by controlling the balance between the attractive and repulsive forces, the authors were able to assemble colloidal nanostructures with diverse ranges of different morphologies and symmetries. When the force balance was symmetric, the assembled colloids showed symmetric overall morphologies. The asymmetric force balance led to

asymmetric morphologies. It is highly intuitive that a careful manipulation of optical tweezers can even generate external force–induced asymmetric packing of colloidal particles. The colloidal particle (surface charged silica) is their primary building unit. Hence, their elementary building blocks (which consist of a couple of colloidal particles) are the primary aggregate (secondary building units), which assembles into the colloidal crystals. Thus, their colloidal crystals are the secondary aggregates (for definitions of and details about these assembly terms, see Chapter 4). As can be expected from the concept of force balance, when they increased the attractive force between the building units, the colloidal crystals they obtained showed more robust and stable properties.

The next system is so-called *dip-pen lithography* printing. An atomic force microscope (AFM) tip is first dipped into the solution of alkanethiol building units. Then, it is carefully moved on the surface of gold substrate to create the intended pattern. Self-assembly of alkanethiol building units with the gold surface creates surface nanostructures. No carving out of building units is involved, which makes this a bottom-up approach. The last system uses a sol of tetramethylorthosilicate (TMOS) with alkyltrimethylammonium bromide (ATAB). It is sprayed through a nozzle whose size is controlled. By allowing the hydrolysis and condensation in the air when they are at the form of aerosol, the mesoporous silica hollow sphere with a well-controlled polydispersity can be obtained. Nozzle does not carve out any building unit. It only provides a spatial constraint which directs the assembly.

13.3.4. Top-Down Approach

Figure 13-5 shows how the top-down approach works for nanofabrication. Lithography is the first example. Different types of lithography are available including optical, electron beam, and X-ray based. Whatever type is in use, the fundamental way to operate lithographic techniques to create nanostructures is carving out the bulk starting materials with a focused high energy source. By operating the hardware with a resolution that is in most cases achievable up to the nanometer range, the desired nanostructure can be obtained. Shown in the figure is the gold surface carved out in a systematic manner so that a patterned gold surface can be obtained. This nanofabricated system can have diverse applications, including in optical devices.

Etching is another popular top-down technique. Different types of etching are widely in use. A key difference from lithography is that etching usually uses chemical means to carve out the bulk starting materials instead of optical means. Strong acids such as hydrofluoric acid and strong bases such as sodium hydroxide are among those used to chemically oxidize out the selected part of the bulk materials. Plasma- or laser-induced etching is also widely in use. The precision of masks often determines the resolution of the pattern created, and it is achievable up to tens of nanometers. Shown in the figure is the fabrication of silicon substrate by etching, which is useful to obtain patterned semiconductor-based devices. Fabrication of nanonails by etching on silicon wafer provides a good related example (Ahuja et al., 2008). These nanonails show the transition from the superlyophobic state to

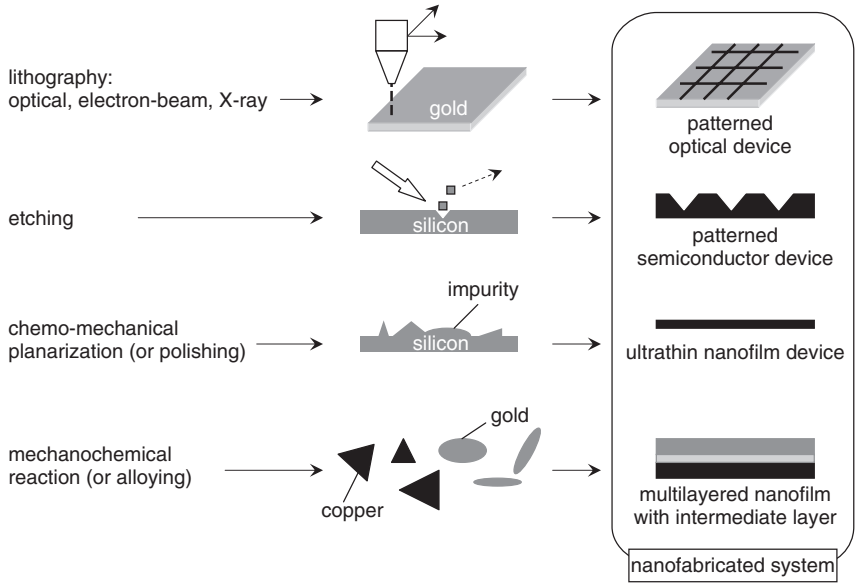


Figure 13-5. Top-down approach to nanofabrication.

wetting when applying an electric field. It is helpful in this regard to revisit the hierarchically patterned surface shown in Figure 11-8.

The third example is a purely mechanical technique. Chemo-mechanical planarization (or polishing) grinds away unnecessary parts from the surface of the bulk starting materials to obtain a satisfactory degree of surface roughness. It is also useful in removing foreign materials or impurities from the surface of the bulk materials. One advantage of this technique is that it does not need any chemical process or optical high energy source, which in many cases require high-cost apparatus and careful setup to meet the resolution requirement while avoiding possible damage to the area that should not be affected by the process. The downside is that the fabrication systems that can use this technique are limited. There are many systems that are too hard, too soft, or too delicate to be processed with this technique. Resolution can be achieved up to tens of nanometers. Shown in Figure 13-5 is a silicon substrate whose surface is polluted by impurity and its own irregular roughness. By proper polishing with a grinder, ultrathin nanofilm can be fabricated with its surface roughness within satisfactory levels.

The last example is similar to the third one. It is also purely a mechanical technique, but not limited on surfaces. A mechanochemical reaction (or bulk alloying) physically mixes two or more different bulk starting materials together to come up with products with different morphologies and compositions. Shown in the figure are pieces of copper and gold bulk starting materials that are mechanically alloyed together. By controlling the degree of mixing along with its direction, a multilayered nanofilm whose intermediate layer is gold-copper alloy can be obtained. The resolution can also be up to tens of nanometers.

13.3.5. Bottom-Up/Top-Down Hybrid Approach

Figure 13-6 shows the bottom-up/top-down hybrid approach to nanofabrication. Literally, this fabrication process employs both the bottom-up and top-down principles to obtain nanofabricated systems. Top-down techniques are always involved to carve out some part of the bulk materials. Depending on the system, top-down techniques are often used to perform one-by-one manipulative assembly, too. An important advantage of this hybrid approach is that it combines the merits of both bottom-up and top-down approaches, that is, the *effectiveness* of the assembly from the bottom-up approach and the *precision* of the fabrication from the top-down approach.

The first example is *micro-contact printing*. Polydimethylsiloxane (PDMS) is first fabricated to have well-defined microstructures. Mostly this can be done by etching. This fabricated PDMS is used as a "stamp" for the mass creation of the patterned structure whose dimension is replicated by the one on PDMS. Alkanethiol (AT) solution can be dipped into and transferred onto the gold surface by this PDMS stamp. Self-assembly of alkanethiol on the gold surface forms the self-assembled monolayer (SAM) of alkanethiols only on the area contacted by the PDMS stamp. Therefore, this is a bottom-up approach. When the PDMS stamp is removed, a nanofabricated system of gold whose surface is regularly patterned with alkanethiols is obtained. This particular fabrication is especially useful in performing rapid multiple copying of self-assembled monolayer.

The second example is *etching-then-SAM formation*. Silicon carbide is a widely used semiconductor material. Etching can carve it out selectively so that a structure with a sharp edge can be created. This sharp edge can, if it is properly modified with organic building units, provide the possibility to change and control the semiconductor properties. By combining this with the masking technique, whenever necessary, alkanethiol can assemble on the structured side of silicon carbide.

The third example has almost the same principles as the second one. It fabricates a *capillary channel array*. Silicon surface is first patterned to have a well-designed surface channel network. Lithography usually works better than etching for carving out of the surface when it needs to work in a continuous manner. In addition, by combining it with the masking technique, alkanetriethoxysilane (AS) can selectively assemble on the area not carved out. This self-assembled monolayer around the capillary channel provides a hydrophobic barrier for the fluid that flows inside the channel. It can also change the flow dynamics of the fluid by controlling the density gradient or compositional inhomogeneity of the self-assembled monolayer. This type of nanofabricated system can be useful as bio-chips or microfluidic devices.

The next example begins with *indium tin oxide (ITO) glass*. Zinc phthalocyanine (ZnP) is deposited on this ITO glass first. Through the same type of assembly, silver vapor is then deposited on top of the ZnP layer. A careful etching can divide this ITO-ZnP-silver multilayered film into small pieces, which can provide the mass production of solar cell devices.

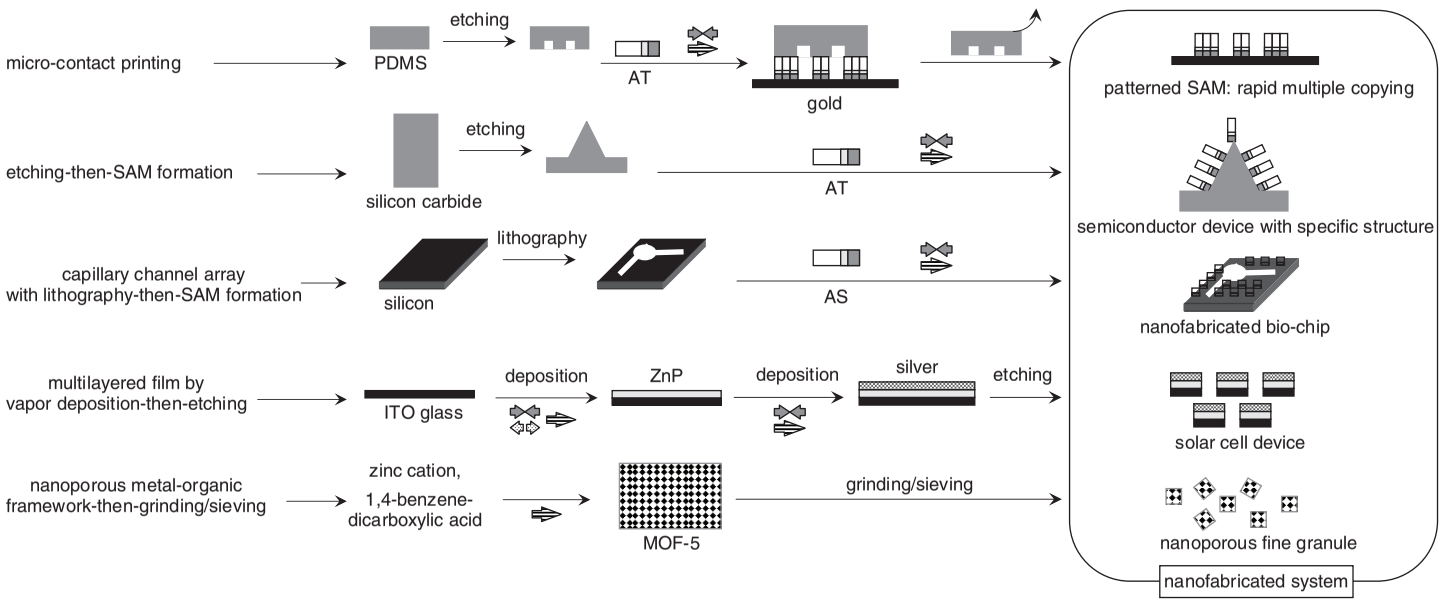


Figure 13-6. Bottom-up/top-down hybrid approach to nanofabrication. SAM is short for self-assembled monolayer.

The last example begins with the assembly of a *metal-organic framework*. Some facts about this material, including why this assembly can be viewed as a bottom-up approach, were explained in Figure 13-2(f). MOF-5 obtained from zinc cation and 1,4-benzenedicarboxylic acid is a bulk material. Grinding/sieving can turn it into a fine granule, which can help maximize the effectiveness of its potential. For example, its use as an adsorbent for hydrogen gas can be maximized in this way through the maximum exposure of its nanopore. The commercialization of MOF materials is now well underway ("Heading to Market with MOFs," 2008).

Case Study 13.3

The similarities and differences between metal-organic frameworks and mesoporous materials are worth mentioning here with some additional details. Mesoporous materials' pore sizes are relatively bigger than metal-organic frameworks so that large molecules can diffuse inside of them. This makes them useful in many applications dealing with large molecules. The sizes, shapes, and arrangements of their pores can be controlled over a wide range, and their inner surfaces can be easily functionalized with a variety of organic and inorganic molecules. But their inner walls are not crystalline, which makes their hydrothermal stability relatively low. This can limit their applications under a solution-based condition. Surface areas range from a couple of hundreds to ~1,500 m^2/g.

Meanwhile, metal-organic frameworks are a crystalline material, thus their stability is high (Férey, 2008; Mueller et al., 2008; Rowsell and Yaghi, 2004). Their capability for the storage of hydrogen gas is remarkably high, which could make them a good storage device for hydrogen fuel. Different organic ligands can give different functionalities to them. Pore sizes of metal-organic frameworks are small (a few nanometers) compared with those of mesoporous materials. Only small molecules can diffuse inside of them. Pore sizes can be controlled, but not the pore shapes and arrangements—at least they are not as flexible as those of mesoporous materials. Inner surfaces cannot be easily modified, at least not by post-synthetic treatments. Regarding the aspect of synthesis, it is advantageous compared with mesoporous materials since no templates are needed. Surface areas easily reach to a couple of thousands m^2/g. One of their recent family members, MOF-210, even shows ultrahigh porosity with 10,400 m^2/g of surface area (Furukawa et al., 2010). There is a general similarity between metal-organic frameworks and mesoporous materials. They both have high inner surface areas, they both have diverse components (for mesoporous materials, silica, titania, zirconia, ceria, and many more; for metal-organic frameworks, numerous choices of metal cations and organic ligands), it is relatively easy for both to expand their production to industrial scale, and, finally, both seem environmentally friendly.

Case Study 13.4

Case Study 8.1 for a forced assembly, shown in Subsection 8.3.2.1 (Warren et al., 2008), nicely demonstrates a bottom-up/top-down hybrid approach to nanofabrication. The nanocomposite of platinum nanoparticle with block copolymer was

first assembled through a forced assembly. This is a typical bottom-up approach. It then underwent a plasma etching to remove the organic component, which left a mesoporous platinum with large, regularly arranged pores. This is a typical top-down approach.

Case Study 13.5

Fabrication of cobalt nanoparticle superlattices that display spin-dependent electron transport (Black et al., 2000) is another good actual example that shows the effectiveness/precision of the hybrid approach. The cobalt building units (cobalt nanoparticles covered with oleic acid molecules) were first assembled into an ordered array via evaporation-induced assembly. Electron beam lithography was then used to fabricate the nanoscale electrodes on top of the nanoparticle array. (This was also Case Study 12.2 for the individual type of nanoproperty, shown in Subsection 12.3.4.)

Case Study 13.6

Fabrication of ultrathin and ultrasmall inorganic light-emitting diodes (ILED) into display and lighting systems in either flat or wavy configurations has been accomplished via the combination of printing-based assembly with photolithography and electron beam evaporation (Park et al., 2009). This work beautifully demonstrates the practicality of the hybrid approach, which yields new design options that are unavailable with either the bottom-up or top-down approach alone. It further shows the importance of the careful design of intermolecular forces (van der Waals force in this case) for the stamp printing of large-scale ultrathin device arrays during the bottom-up process.

13.3.6. General Trends

Each nanofabricated system is a unique product of each fabrication system. Each nanoelement of the nanofabricated system is a unique expression of its building units. They can be coupled locally or as a whole. They also can have a synergistic or an antagonistic outcome after the fabrication. All of these aspects have some degree of impact on the nanoelements of the nanofabricated systems. For some cases, different nanofabrication processes become the major reason for differentiating the nanoelements, even though the nanofabricated system might be the same. Figure 13-7 shows a general trend of nanofabrication that covers these aspects from the three approaches.

The mass assembling capability of nanofabrication becomes critically important when it goes to industrial scale. Generally, this capability is enhanced where fabrication is performed based on the bottom-up or the bottom-up/top-down hybrid approach. Because of the technical difficulties of top-down techniques and the limitations of the starting bulk materials that are comparable to them, the diversity of building units is much increased when the bottom-up or the hybrid approach is used. More diverse building units mean more diverse nanofabricated systems and

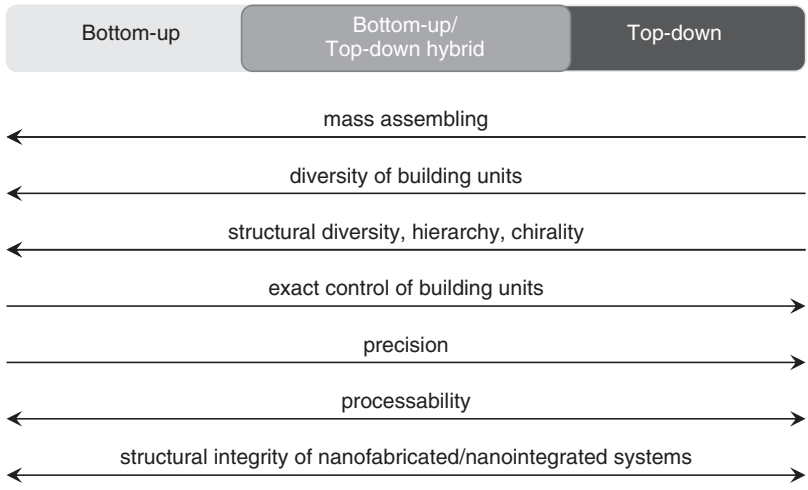


Figure 13-7. General trend of the three main approaches to nanofabrication.

more diverse nanoelements that can be explored. Structural diversity, hierarchy, and chirality are also important for widening the practicality of the nanofabricated systems. As discussed in the second part of the book, these factors are closely related to the structural design of the building units. It thus is easier to take advantage of them with a bottom-up or hybrid approach.

Exact control of the building units is useful when the nanoelement is determined by the local control of a few key building units. Hence, the top-down approach provides an advantage for this. Generally, the top-down approach has higher precision because of capability of manipulative assembly. Processability means ease of the fabrication. This factor is important because it determines how practical a specific fabrication can be. It is, however, very much dependent on each nanofabrication system.

Another factor is the structural integrity of the nanofabricated systems. It might appear that top-down processed systems would have better structural integrity because they are the products of the bulk materials. But structural integrity is measured not by the absolute strength of the nanofabricated systems but by their relative stability during actual use. As long as they perform the desired functions at given conditions, arguments about their absolute strength are less meaningful. Pure bottom-up fabrication in many cases provides enough, sometimes surprisingly strong, structural strength and resilience for nanofabricated systems to make them function properly even under harsh conditions.

Case Study 13.7

A study (Kawai et al., 2009) that shows the self-healing power of self-assembled system provides a good argument for this aspect. A self-assembled molecular wire of cyanoporphyrin was first formed on solid surface. This wire was easily

cut when an additional repulsive force was imposed by the tip apex of dynamic force microscopy. This should come as no surprise since the wire was assembled through the balance between intermolecular forces. The damaged wire quickly recovers its original shape at room temperature. This feature of self-assembly, disassembly (damaged by external shock), and self-reassembly of assembly systems has important implications for the fabrication of reliable nanofabricated systems and for their functions.

13.4. COLLECTION OF TOP-DOWN TECHNIQUES

Table 13-1 lists the top-down techniques that are widely in use. Some of them were already shown in Figure 13-2(e). Indentation is a mechanical process that is performed by atomic force microscopy. Photolithography and etching are the two most popular techniques used in semiconductor device fabrications. Based on how they etch out the bulk materials, etching techniques have many derived names.

13.5. COLLECTION OF TOP-DOWN BULK MATERIALS AND FUNCTIONALIZING AGENTS

Table 13-2 lists the bulk materials that are widely used in the literature for nanofabrication. In principle, this list should be limitless. A large number of bulk materials are proven to be effective for the fabrication of nanofabricated systems. This table tries to be a comprehensive one, but certainly does not cover them all. Figure 13-2(d) showed some of them. And Table 2-8 listed most of them.

Table 13-3 collects the assembly building units that are widely applied in the literature for functional modification of nanofabricated systems. They primarily

TABLE 13-1. Collection of top-down techniques.

Instrument/Process	
atomic force microscope (AFM)	
scanning tunneling microscope (STM)	
indentation	
mechanical grinder, sieve (mesh)	
optical tweezers (OT)	
photolithography	
etching:	dry
	wet
	plasma
	electrochemical
	photochemical
	photoelectrochemical
	electron-beam sputter
	ion-beam sputter
	laser-enhanced sputter
	UV-enhanced sputter

TABLE 13-2. Collection of bulk materials that are used for nanofabrication.

Chemical/Class Name
Most of the substrates in Table 2-8
polydimethylsiloxane (PDMS)
polyimide
polystyrene
acrylic polymers
polycarbonates
semiconductor materials
teflon
fluoropolymers
resins
photoresists

TABLE 13-3. Collection of assembly building units that are used for functional modification of nanofabricated systems.

Building Unit
Most of the self-assembly building units in Table 1-9 (composed of attractive (**A**) and conditional directional ($\mathbf{D}^c$) segments)
Most of the ligands for the fabrication building units in Tables 2-4 and 2-5
Most of the reactive building units in Table 2-7

functionalize the surface of the nanofabricated systems. But the impact of modification often changes the functions of the entire system. As with the bulk materials in Table 13-2, this list in principle is limitless. A large number of building units of different types are proven to be effective as functionalizers. Tables 1-9, 2-4, 2-5, and 2-7 are more comprehensive lists.

13.6. COLLECTION OF NANOFABRICATED SYSTEMS AND THEIR APPLICATIONS

Table 13-4 collects the nanofabricated systems that frequently appear in the literature. A key nanostructure and nanoproperty for each nanofabricated system is also shown. The fabrication approach for each system is not specified in this table. Most of them are fabricated by the bottom-up/top-down hybrid approach. But many of them can be fabricated by other approaches, too. Applications are also included. Many of these are potential, and some of them are already in use.

13.7. SUMMARY

This chapter showed how to design effective nanofabrication for each nanofabricated system. Three main approaches to nanofabrication, that is, bottom-up,

TABLE 13-4. Collection of nanofabricated systems, and their key nanostructures, key nanoproperties, and applications.

Nanofabricated System	Key Nanostructure	Key Nanoproperty	Application
field effect transistor	nanopatterned semiconductor multilayer	dielectric permittivity and conductivity	nanoelectronics, microelectronics
optoelectrofluidic device	nanopatterned channel on solid/polymer surface	capillary flow, diffusion, electrokinetics	biomedical devices, analytical devices
microfluidic device	micropatterned channel on solid/polymer surface	capillary flow, diffusion	biomedical devices, analytical devices
nanofluidic device	nanopatterned channel on solid/polymer surface	capillary flow, diffusion	biomedical devices, analytical devices
lab-on-a-chip device	integrated micro-/nano-patterned channel/reservoir on solid/polymer surface	capillary flow, diffusion, confined mixing/reaction	biomedical devices, analytical devices
MEMS (microelectro-mechanical system)	micropatterned/etched/integrated semiconductor chip	electrical/mechanical properties in microscale	sensors, actuators, switches
NEMS (nanoelectro-mechanical system)	nanopatterned/etched/integrated semiconductor chip	electrical/mechanical properties in nanoscale	sensors, actuators, switches
silicon-on-insulator device	semiconductor multilayer	capacitance	microelectronics
charge transfer device	patterned semiconductor multilayer	controlled charge flow	microelectronics
liquid crystal display (LCD) device	sandwiched liquid crystal within patterned microspace	optical/electrical properties	microelectronics
light emitting diode (LED) device	microfabricated/multilayered III-V semiconductors	electroluminescence	microelectronics
organic light emitting diode (OLED) device	microfabricated/multilayered organics/polymers	electroluminescence	microelectronics
plasma display device	sandwiched plasma within patterned microspace	electroluminescence	microelectronics
surface acoustic wave device	micropatterned solid with piezoelectric materials	acoustic wave on solid surface	filter, oscillator, transformer within microelectronics

magnetic memory storage device	micropatterned magnetizable materials	magnetization, ferromagnetization	data storage in microelectronics
optical memory storage device	micropatterned optically-active materials	optical selection	data storage in microelectronics
optoelectronic device	microfabricated/multilayered semiconductors	quantum mechanical effect of light	microelectronics
photoelectric device	microfabricated/multilayered semiconductors	photoelectric effect	electronics, solar cells, sensors
photoconductive device	microfabricated/multilayered semiconductors	photoconductive effect	electronics, solar cells, sensors
photoresistor device	microfabricated/multilayered semiconductors	photoresistor effect	microelectronics
photovoltaic device	microfabricated/multilayered semiconductors	photovoltaic effect	electronics, solar cells, sensors
piezoelectric device	layered nonconducting crystal	piezoelectricity	electronics, communication devices
heterojunction device (quantum-well device)	bilayered dissimilar crystalline semiconductor	electronic energy band	electronics, lasers, solar cells
spin-valve device	microfabricated/multilayered nano-carbon/ferromagnetic electrode	magnetoresistance	memory devices
thermoelectric device	microfabricated/multilayered metals/metal oxides	thermoelectricity	batteries, convertors, generators
electrochemical device	microfabricated/multilayered metals/metal oxides	electrochemical response	analytical devices, sensors

top-down, and bottom-up/top-down hybrid approaches, were introduced and correlated with the nanostructures and nanoproperties. We have seen that:

1. Nanofabricated systems can be effectively fabricated when self-assembly principles and top-down techniques are properly combined together.
2. This involves not only assembly building units but diverse bulk materials as well.
3. The three approaches to nanofabrication are not absolute; they are flexible and interchangeable depending on each nanofabricated system.
4. Applications of nanofabricated systems are primarily determined by the key nanostructures and nanoproperties that each system expresses.

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14

Nanomechanical Movements: Combined to Operate

14.1. NANOISSUE

As described in the previous chapter, nanofabricated and nanointegrated systems can be effectively fabricated via a well-designed nanofabrication. These nanotechnology systems find practical use in the macroworld. They are designed with the capability of bringing the uniqueness of the nanoworld into the macroworld. The expression of this uniqueness can solely originate from the nanoworld. It can be a result of the synergistic cooperation with the macroworld. It also can be a result of antagonistic interaction with the macroworld in a useful way. The scope of nanofabricated and nanointegrated systems is wide and diverse. Among those, there are systems whose functions are so unique that they deserve to be viewed as a separate group. Some of the nanofabricated systems have the capability of performing unique functions whose mechanical operations resemble those in the macroworld. These functions are called *unit operations* (Lee, 2008). And those nanofabricated systems that have the capability of unit operations are called *nanodevices*. Likewise, some of the nanointegrated systems have the capability of conducting unique functions such that their interactions with the macroworld can be viewed as effective communication with the macroworld. These nanointegrated systems that have the capability of communication with the macroworld are called *nanomachines*. Clear boundaries between nanodevices and nanomachines and the rest of the nanofabricated and nanointegrated systems cannot be definitively drawn. However, nanodevices and nanomachines play a large part in nanofabricated and nanointegrated systems.

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Table 2-3 and Figure 2-9 have the details for this aspect. As the final chapter of this application part, the goal here is to connect nanofabrication with the development of nanodevices and ultimately with nanomachines. Thus, the main question is:

How can the most effective nanofabrication process be designed for a specific nanodevice?

It can go further:

How can the building units be chosen for a specific nanodevice?

How can the concept of force balance be used to understand the working mechanisms of nanodevices?

14.2. GENERAL OVERVIEW

Figure 14-1 is a general overview of the design of nanodevices. The concept of unit operation is the key to the function of nanodevices, and three element motions govern the unit operations. This is briefly revisited in the next section.

Nanofabrication for the design of nanodevices was briefly introduced in Figure 13-1. In some cases, the nanofabricated systems in the figure are actually nanodevices. Also, in some cases, nanodevices can be obtained via proper nanofabrication of nanofabricated systems. Nanodevices can be often converted into nanomachines via nanofabrication.

The first step is to identify the nature of the nanodevice and/or nanomachine to be fabricated. Since nanodevices and nanomachines are a part of nanofabricated and nanointegrated systems, the identification of their functions should make it possible to use Figure 13-1 to determine the right nanofabrication. This nanofabrication is performed in the next step. What makes the nanodevices different from the rest of the nanofabricated systems is their capability of performing unit operations. Once the nanodevice is fabricated, it should be tested for an intended unit operation. If it does not satisfy the unit operation requirement, the process should go back to identify other nanofabrications. What is important during this process is to rebalance and modify the three element motions so that the nanodevice can have a proper unit operation. If the answer to the first question is yes, the next step is to characterize the nanodevice as a whole. If this does not satisfy the initial purpose, the nature of the nanodevice should be adjusted or re-identified. Once the nanodevice shows a unit operation and satisfies an intended application, and when there is a requirement for a nanomachine, the process can continue. This is a nanofabrication to integrate two or more nanodevices into one system. Depending on the requirement, non-nanodevice nanofabricated systems can be a part of this fabrication. What makes the nanomachines different from the rest of the nanointegrated systems is their capability to communicate with the macroworld. If the nanomachine does not show this capability, the process should identify other nanofabrications. As in the nanodevice fabrication, modification of the three element motions is the key during this cycle. If the answer is yes, the nanomachine should be characterized as a whole.

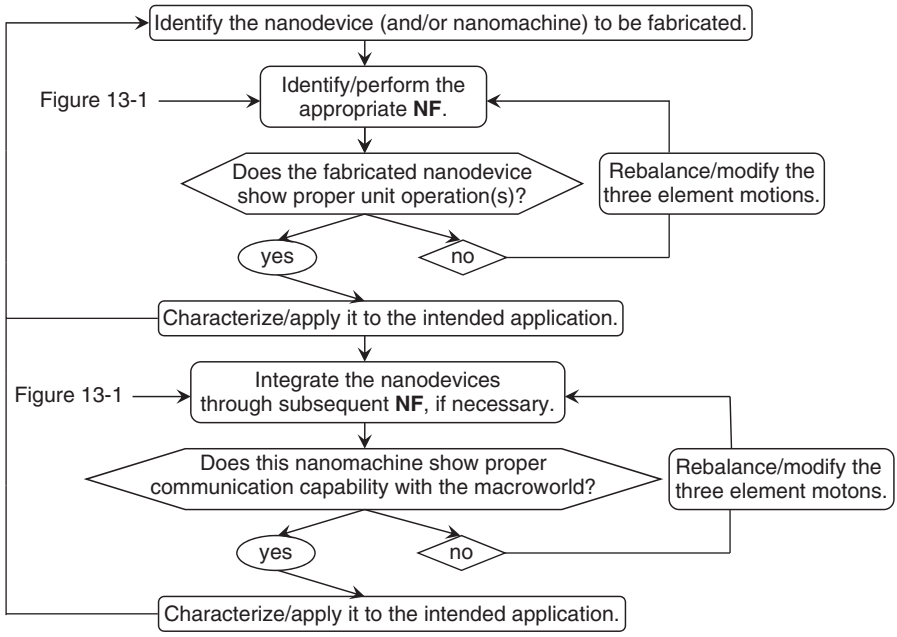

Identify the nanodevice (and/or nanomachine) to be fabricated.
Figure 13-1
Identify/perform the appropriate NF.
Does the fabricated nanodevice show proper unit operation(s)?
Rebalance/modify the three element motions.
yes
no
Characterize/apply it to the intended application.
Figure 13-1
Integrate the nanodevices through subsequent NF, if necessary.
Does this nanomachine show proper communication capability with the macroworld?
Rebalance/modify the three element motons.
yes
no
Characterize/apply it to the intended application.

Figure 14-1. General overview of the design of nanodevices. **NF** is short for nanofabrication.

14.3. FABRICATION PRINCIPLES

14.3.1. Element Motions

With a few exceptions, all nanodevices have at least one moving component somewhere within their systems. Moving components are composed of individual assembly building units, and their operating range is mostly within the nanometer scale or below. The types of moving components and their actions are seemingly complicated and random. However, the concept of three element motions between the building units categorizes them in a systematic manner.

Figure 14-2 shows the three element motions. They are a push motion, a pull motion, and a guide motion. A push motion is the motion between the building units of the moving component where one of the building units moves as if it were being pushed by the others within the component. Often, two or more building units move as if they were being pushed by the rest of the building units. A pull motion is the opposite situation. It is the motion between the building units within the moving component where one of the building units moves as a result of the pulling action by the others. As in the push motion, two or more building units are often being pulled by the rest of the building units. A guide motion is the motion between the building units within the moving component that has the capability of directing the push and/or pull motions of a certain building unit or building units. The operations of most of the moving components can be understood as one, or a combination of two or all three, of these element motions.

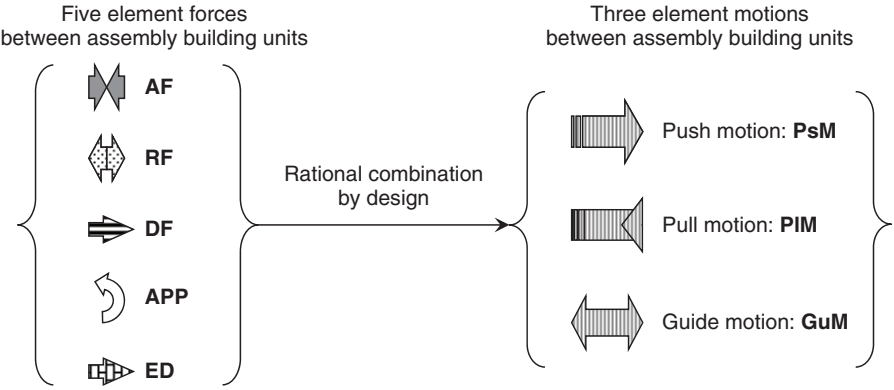


Figure 14-2. Three element motions of nanodevices are generated by the vectorial sum of the five element forces between assembly building units. **AF, RF**, and **DF** refer to attractive, repulsive, and directional forces, respectively. **APP** and **ED** refer to asymmetric packing process and external force–induced directional factor, respectively.

The origin of the three element motions is the five element forces between the building units (see Figure 2-2 for the details). These are the attractive force, repulsive force, directional force, asymmetric packing, and external force–induced directional factor. Whenever the building units are fabricated into a moving component, the moving component should always be designed in such a way that at least one or more of the five element forces remain (or are newly generated as a result of the fabrication) and interact between the building units. The sole action of a single element force, or the vectorial sum of two or more of the element forces, generates the element motions. This in turn suggests that a rational combination of the five element forces is the key to the design of the element motions. Figure 14-2 also provides the symbols representing each element motion. These are used for the rest of this chapter.

14.3.2. Working Mechanisms

Figure 14-3 shows that the working mechanisms for the unit operations can be classified into six different types based on the concept of three element motions. *Type I* is a working mechanism that is generated only by a push motion. A periodic repetition of push motions between the building units induces a constant movement. A guide motion is not involved. Depending on the configuration between the building units, it can look like either a directional movement or almost a random-wise movement. The push motion can operate between two or more movable building units or between movable and static building units.

Type II is a working mechanism that is generated only by a pull motion. A periodic repetition of pull motions between the building units induces a constant movement of one or more building units. As with Type I, no guide motion is involved, and both movable and static building units participate.

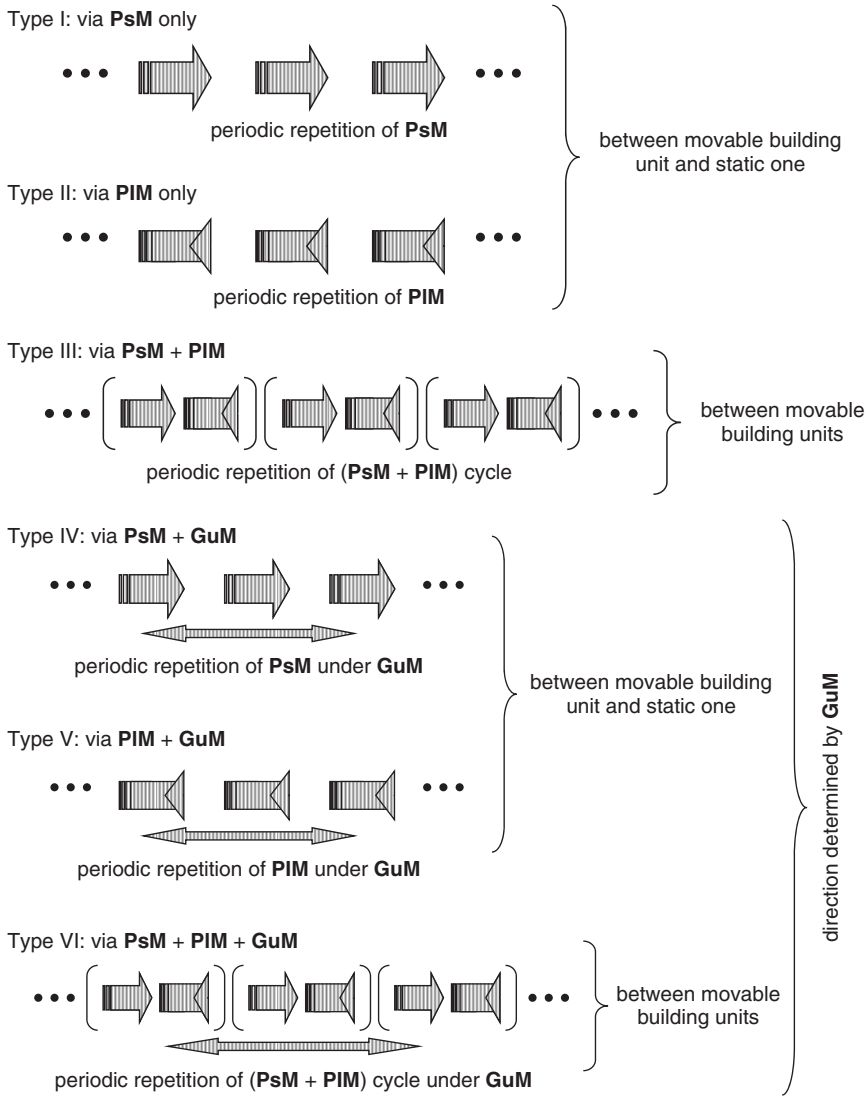

Type I: via **PsM** only
periodic repetition of **PsM**
Type II: via **PIM** only
periodic repetition of **PIM**
between movable building unit and static one
Type III: via **PsM** + **PIM**
periodic repetition of (**PsM** + **PIM**) cycle
between movable building units
Type IV: via **PsM** + **GuM**
periodic repetition of **PsM** under **GuM**
Type V: via **PIM** + **GuM**
periodic repetition of **PIM** under **GuM**
between movable building unit and static one
Type VI: via **PsM** + **PIM** + **GuM**
periodic repetition of (**PsM** + **PIM**) cycle under **GuM**
between movable building units
direction determined by **GuM**

Figure 14-3. Six different types of working mechanisms for the unit operations of nanodevices. **PsM, PIM**, and **GuM** refer to push, pull, and guide motions, respectively.

Type III is a working mechanism that is generated by a periodic repetition of push–pull motion cycles. This can be either a periodic movement or a gradual movement with a given directionality, depending on the actual configuration between the building units. No guide motion is involved. This working mechanism usually operates between the movable building units.

Type IV is a working mechanism that is generated by the combination of push and guide motions. The periodic repetition of push motions is similar to type I.

But it always operates under the guide motion. This therefore always has certain directionality. As with types I and II, this working mechanism operates between two or more movable building units, with or without static building units.

Type V is a working mechanism that is generated by the periodic repetition of pull motions under the guide motion. The rest is the same as for type IV.

A *type VI* working mechanism is generated by the periodic repetition of push–pull motion cycles under the guide motion. This usually operates with the movable building units, and always has certain directionality. But the actual movement can be either periodic or unidirectional, depending on the configuration of the push and pull motions.

14.3.3. Analysis of Building Units

Figure 14-4 shows nanoassembly building units (for details, see Section 2.2) that are used for the fabrication of nanodevices in this chapter. As in Figure 13-2, the symbols for each type of building units come from Figure 2-1; rectangular and circular symbols are used for molecular and colloidal building units, respectively.

Figure 14-4(a) has molecular self-assembly building units. ω-mercapto alkanoic acid homologue series have a long hydrocarbon chain connected with thiol and carboxylic acid groups at each end of them. As long as this hydrocarbon chain is long enough that it can induce an attractive hydrophobic force, it has no problem acting as an attractive segment. The roles of the two functional groups are somewhat different from those of α,ω-alkanedithiols in Figure 12-2(a) and from those of ω-mercaptoalkane trimethoxysilanes in Figure 13-2(a). The thiol group has the capability to be a directional segment with some limitation. The carboxylic acid group, on the other hand, has the clear capability to be a directional segment. Table 1-8 showed more details for this aspect.

The same logic is applied for the next building unit, alkanoic acid, ω-(triethoxysilyl)-. As long as the hydrocarbon chain is long enough, it should be assigned as an attractive segment. The triethoxysilyl and carboxylic acid groups are conditional directional and directional segments, respectively.

The third building unit is somewhat unusual. It is the synthetic product of four fullerene molecules with a linear-shaped organic stem. Its detailed synthesis and structure are reported by Shirai et al. (2006). As shown in Figure 12-2(a), fullerene can be viewed as a molecular self-assembly building unit. Figure 12-2(a) therefore assigned the attractive segment for it. The repulsive segment was negligible. This analysis is valid for this so-called "fullerene-wheeled compound." It has an attractive segment with a negligible repulsive segment. One characteristic feature of this particular building unit comes from its geometrical configuration. The four fullerene molecules are attached on the main stem. It is as if the four wheels were attached on a car frame, which ensures the proper moving of the car. Therefore, an energetic situation can be induced so that the movement of this building unit, whenever it happens, is favored along a certain direction. The assignment of a directional segment for this building unit is justified from this. But unlike typical intrinsic directional segments, this directional segment has a

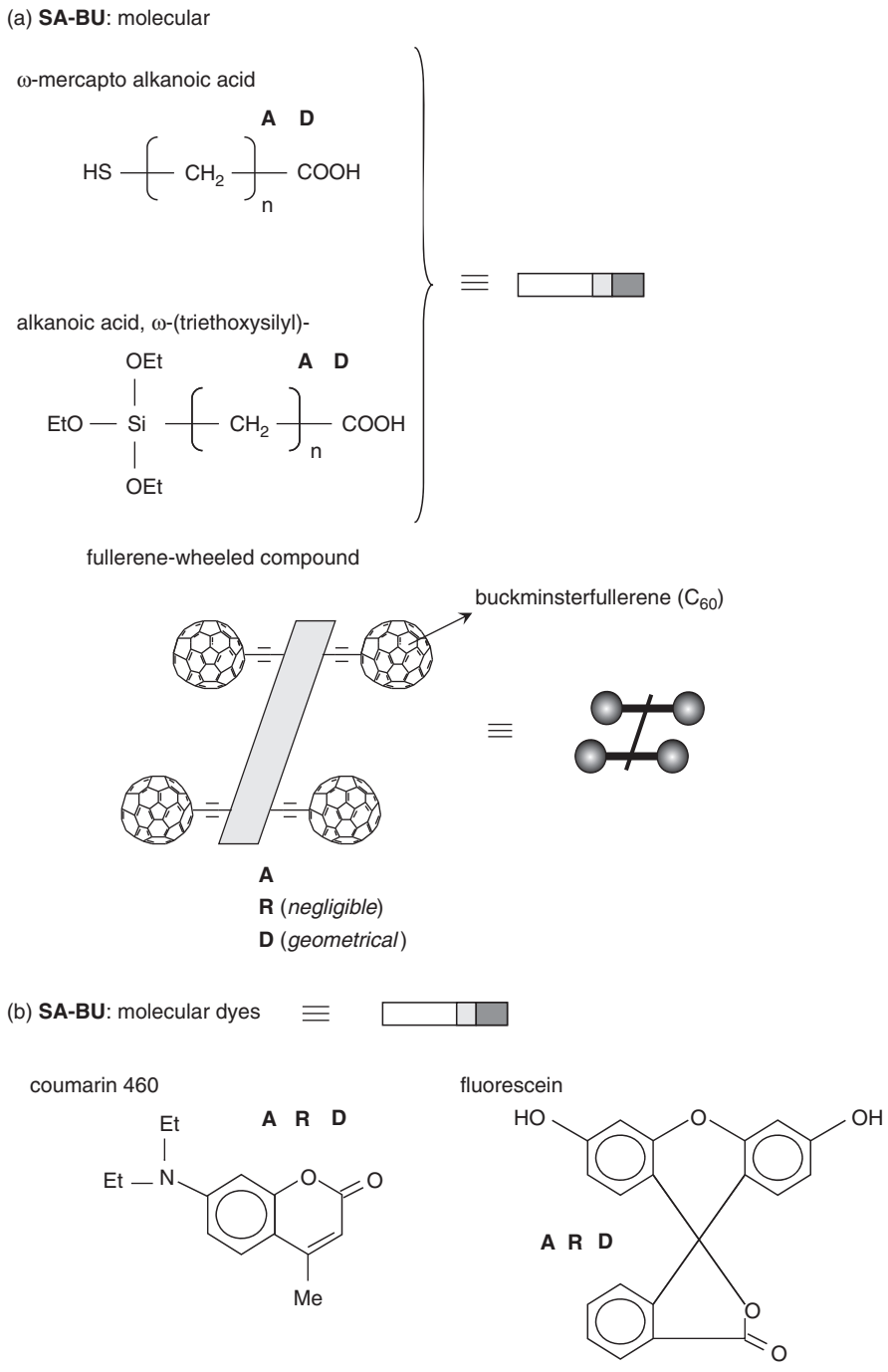
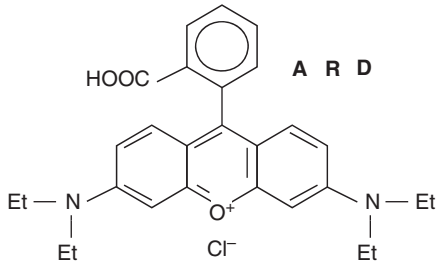
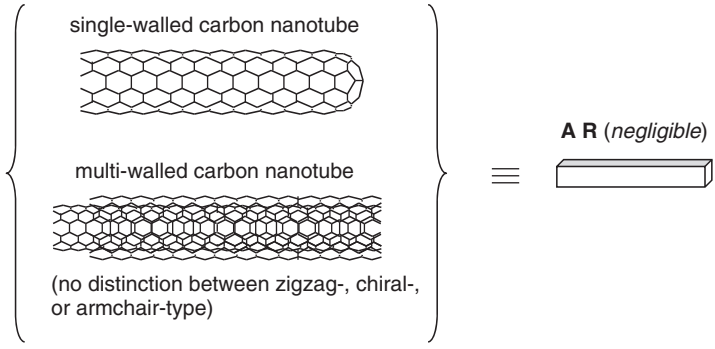


Figure 14-4. Building units. **SA-BU** and **F-BU** refer to self-assembly and fabrication building units, respectively. **A, R, D, AP**, and **EF-F** refer to attractive, repulsive, directional, asymmetric packing, and external force–specific functional segments, respectively.

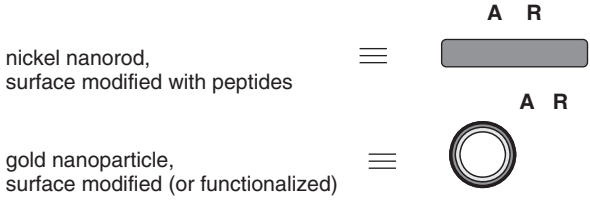
rhodamine B



(c) **SA-BU**: colloidal


single-walled carbon nanotube
multi-walled carbon nanotube
(no distinction between zigzag-, chiral-, or armchair-type)
A R (negligible)

(d) **F-BU**: colloidal



(e) **SA-BU**: molecular, polymeric

poly(*N*-isopropylacrylamide)

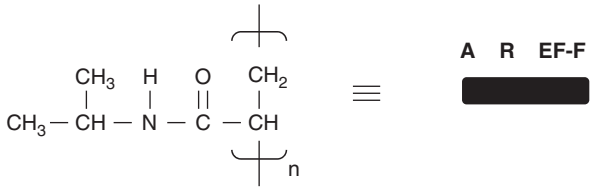


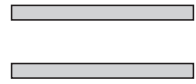
Figure 14-4. (*Continued*)

(f) **SA-BU**: substrate

A R (*negligible*)
D (*conditional*)

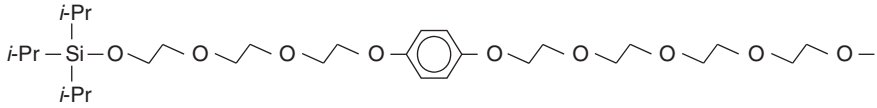
silica nanopore
(or nanogroove)

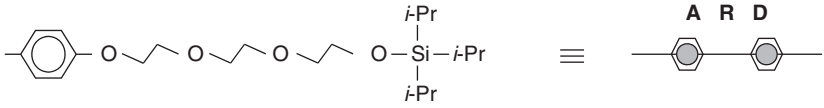
nanochannel;
anodic alumina membrane

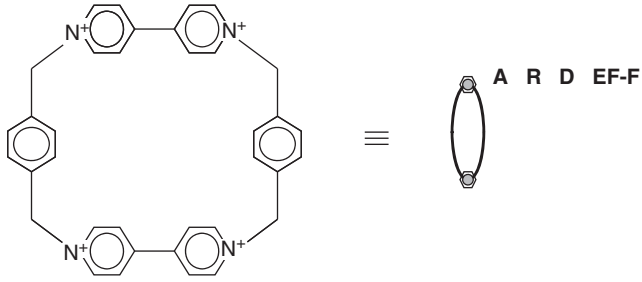


A R (*negligible*)
D (*conditional*)

(g) **SA-BU**: rotaxane-based molecular







(h) **SA-BU**: catenane-based molecular

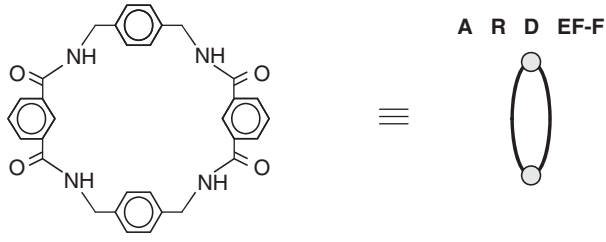
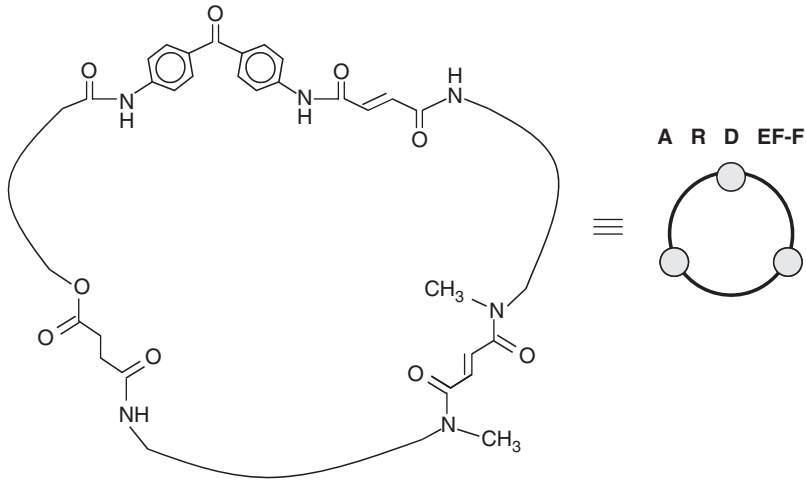


Figure 14-4. (*Continued*)

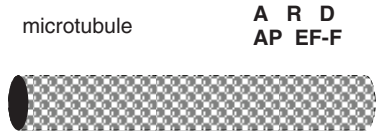


(i) **SA-BU**: biological

cytoplasmic protein: kinesin

This is a schematic structure.

microtubule

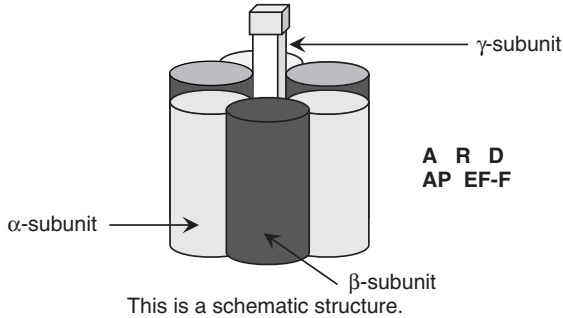


This is a schematic structure.

DNA

(j) **F-BU**: biological

motor protein conjugate:
motor part of F_1-adenosine triphosphate synthase (F_1-ATPase),
β- and γ-subunits modified with peptides



This is a schematic structure.

Figure 14-4. (*Continued*)

geometrical origin. The dimeric-dumbbell-shaped symbol is used for this fullerene-wheeled compound for the rest of this chapter.

Figure 14-4(b) has molecular dye building units. Figure 12-2(a) showed a dye molecule, diindenoperylene, as a self-assembly building unit, which was analyzed to have attractive, repulsive, and directional segments. The three dye molecules here are coumarin 460, fluorescein, and rhodamine B. Their molecular structures are quite different from that of diindenoperylene. However, the impact of the multi-ring parts is still attractive and at the same time directional because of the ring current effect combined with their planar structural feature. Thus, all three dyes here have attractive and directional segments. The van der Waals force provides an additional attractive segment for them. For fluorescein, two hydroxyl groups provide an additional directional segment, thanks to their hydrogen-bonding capability. The carboxylic group in rhodamine B also generates an extra directional segment. The molecular shape was another factor that gave diindenoperylene a directional segment. But the impact of molecular shapes for these dyes is not as prominent as in diindenoperylene. The intrinsic repulsive force, with the same logic as for diindenoperylene, becomes a repulsive segment for all three dyes. Rhodamine B has an electrostatic repulsive segment as well.

Figure 14-4(c) shows two colloidal self-assembly building units. The first one is a single-walled carbon nanotube, and the second one is a multi-walled carbon nanotube. For the second one, no distinction between the three different types, which are zigzag, chiral, and armchair, has been made. Figure 12-2(c) showed the segmental analysis of some colloidal building units. With the assumption of no or minimal surface charges, they have an attractive segment but their repulsive segments are negligible. The two carbon nanotubes here are assumed to be pristine, which means that there is no or minimal surface charge. This makes their repulsive segments negligible. Considering their lengths, which can easily reach over hundreds of nanometers, the van der Waals force is there as an attractive force. This is their attractive segment. The symbol of a square prism is used for brevity. It is intuitive in this regard to refer to a review article that discusses the potentiality of carbon nanotubes for components of nanodevices, and the implication of capillary and van der Waals forces for their realization (Pugno, 2007). The study on the effects of carbon nanotubes on cell viability and proliferation is also worth reading (De Nicola et al., 2007).

Two more colloidal building units, but fabrication ones, are presented in Figure 14-4(d). Nickel nanorod is assumed to have its surface modified with peptides. While van der Waals force is its attractive segment, the repulsive force that is generated by this surface modification makes its repulsive segment. The same analysis can be applied for the gold nanoparticle whose surface is modified with organic molecules. It also has attractive and repulsive segments. Figure 7-2(b) showed more details for the surface modified colloidal particles.

Figure 14-4(e) is a polymeric self-assembly building unit. Shown is a poly(*N*-isopropylacrylamide). Its segmental analysis was shown in Figure 9-8. It has attractive and repulsive segments along with a thermosensitive external force–specific functional segment.

Figure 14-4(f) has two substrates. The segmental structure of silica nanopore is the same as the silicon nanogroove shown in Figure 12-2(d) as long as the assumption of no surface charge is in place. Anodic alumina membrane is another substrate that is widely used when there is need for a well-defined capillary channel. Figure 12-2(d) also had montmorillonite. The spacing between the layers of montmorillonite and the distance between the channels of anodic alumina membrane are quite different. Montmorillonite usually has its spacing about a few tens of nanometers. For anodic alumina membrane, this distance typically ranges from a few hundred nanometers to a few micrometers. However, both have a well-developed confined space that is very directional. With the assumption of no surface charge, the segmental structure of anodic alumina membrane should be the same as montmorillonite except for the electrostatic force–origin repulsive segment. Hence, both substrates shown here have an attractive segment and a directional segment that is conditional. Their repulsive segments are negligible.

Figure 14-4(g) illustrates a pair of rotaxane-based molecular self-assembly building units. More details on their syntheses and structures are reported in Anelli et al. (1991). The two symbols on the right-hand side of the figure are used for the rest of this chapter. The top one has a long linear shape. This particular molecular shape provides a directional segment to this building unit. The two tri(isopropyl)silane groups at both ends become its conditional directional segment. The same logic as for the first two building units shown in Figure 14-4(a) is applied to this. This building unit has three sections of ethylene oxide–based chains. Ethylene oxide chains are usually a typical source of repulsive hydration force especially when they cooperate with a typical attractive segment such as long hydrocarbon chains. For the three ethylene oxide–based chains here, there will be a hydration force generated by them in aqueous solution, which will have to be assigned as a repulsive segment. There is no attractive force generating part here. But the hydrophobic force still can come from the ethylene parts even though it is small. Combined with the role of the two benzene rings, this can be an attractive segment.

The other one is ring-shaped. This geometrical feature first provides a directional segment for this building unit. It also has four rings that are sensitive on solution pH. It thus has an external force–specific functional segment. These functional groups can also induce an electrostatic repulsive force, which makes them a repulsive segment. The two benzene rings can induce an attractive force along with the four methylene groups. Thus, they are an attractive segment of this building unit.

Another pair of self-assembly building units is shown in Figure 14-4(h). They are catenane-based molecules. Details on their structures are reported by Leigh et al. (2003). For brevity, the symbols on the right-hand side are used for the rest of this chapter. For both building units, the same approach as for the second building unit from the previous pair can be used for the analysis of their segmental structures. First, both have a ring-shaped morphology, which provides them a directional segment. In addition, both have a number of amine-based groups, which can be an external force–specific functional segment in aqueous solution when they are properly assembled. At the same time, these groups can generate an electrostatic repulsion when the condition is right. This makes them have a repulsive segment.

Finally, for the building units on top, there are enough benzene rings to provide an attractive force along with four methylene groups. This is its attractive segment. For the other building unit, there are enough hydrocarbon chains that induce an attractive hydrophobic force. This is its attractive segment.

Figure 14-4(i) has three biological self-assembly building units. One of the cytoplasmic proteins, kinesin, is the first one. This is a well-known so-called *motor protein* that has a unique walking capability. It is the result of delicate force balance between its components. Like many other motor proteins, this is sensitive to a particular solution condition: ATP/ADP conversion. The part that is susceptible to this condition is its external force–specific functional segment. Also, it is a protein, which means that it consists of amino acids, which in turn means that it has directional and asymmetric packing segments. With the same logic, it has attractive and repulsive segments as well. Figure 12-2(b) has more discussion about the segmental structure of biological molecules.

Microtubule is the next building unit. Its detailed structural feature is beyond the scope of this section. It usually works complementarily with kinesin to express the walking capability of kinesin with a unique directionality. This part thus becomes its external force–specific functional segment and its directional segment as well. Microtubule is an aggregate of its component proteins. More precisely, it is a self-assembled aggregate that is formed through hierarchical/directional self-assembly of two different self-assembly building units of α- and β-tubulins. This causes it to have attractive, repulsive, and asymmetric packing segments.

Two DNA chains are the third building unit. The sequences for both DNA chains are random. They do not represent any specific function or origin. However, they are selected to complement each other through C-G and A-T interactions so that they can be selectively attracted when they are close. This takes place with certain directionality. Hence, they have an external force–specific functional segment and at the same time a directional segment. With the same logic for kinesin and microtubule, they have attractive, repulsive, and asymmetric packing segments as well. For brevity, the symbols on the right-hand side are used for the rest of this chapter.

Figure 14-4(j) has a motor protein conjugate, the motor part of F_1-adenosine triphosphate synthase (F_1-ATPase). Its details are reported in Nishizaka et al. (2004) and Soong et al. (2000). It is composed of three α-subunits, three β-subunits, and one γ-subunit. The β- and γ-subunits are assumed to be modified with peptides, which makes it a biological fabrication building unit. The driving force for the proper moving (rotation) of this protein conjugate is, as with kinesin and microtubule, a rational combination and alternation of ATP/ADT conversion. Thus, the part that is susceptible to this condition is its external force–specific functional segment. As a protein conjugate, it has an intrinsic asymmetric packing segment that is the key component for its rotation capability. The well-coordinated arrangement of protein subunits is responsible for the directionality of that rotation. This is its directional segment. In addition, as with kinesin and microtubule, it has attractive and repulsive segments as well because it is a protein in the first place.

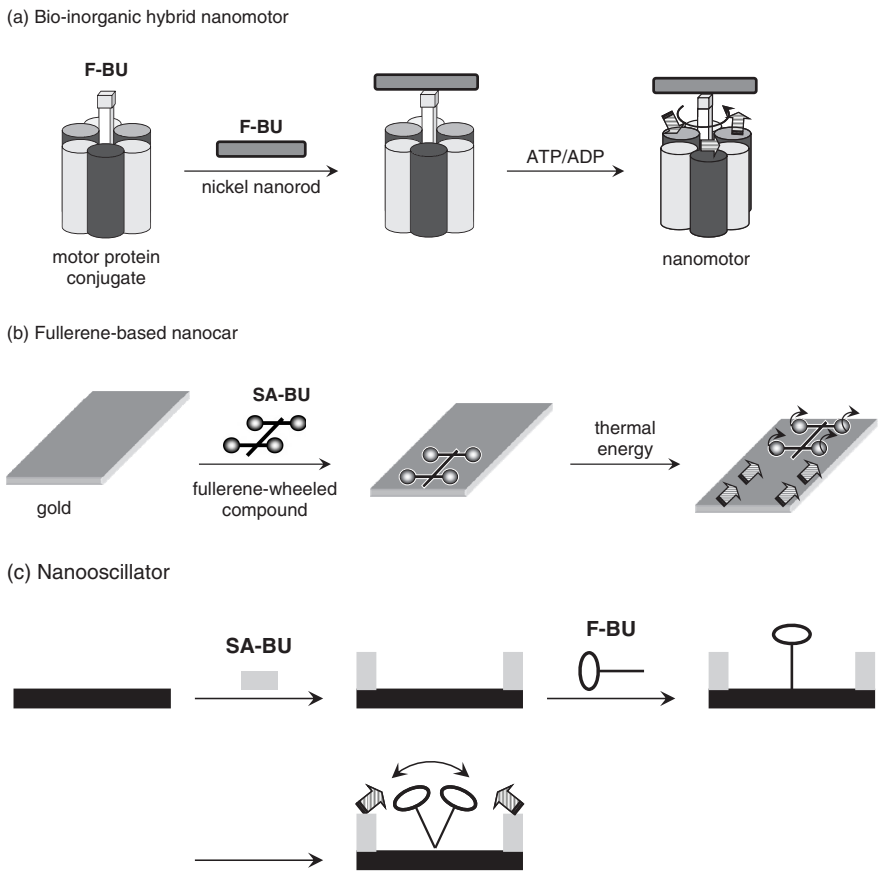


Figure 14-5. Nanodevices that show periodic push motions (type I) of the working mechanism. **SA-BU** and **F-BU** refer to self-assembly and fabrication building units, respectively.

14.3.4. Periodic Push Motions

Figure 14-5 illustrates the nanodevices that show periodic push motions of a working mechanism. The first one is a bio-inorganic hybrid nanomotor. This is fabricated through a selective attachment of nickel nanorod from Figure 14-4(d) on top of the γ-subunit of the motor protein conjugate from Figure 14-4(j) (for full details, see Nishizaka et al., 2004; Soong et al., 2000). With rational control of ATP/ADT conversion, this top part with nickel nanorod can rotate in a unidirectional manner. This is largely the result of the push motions to the γ-subunit generated by $\alpha_3\beta_3$ hexamer at the bottom.

Case Study 14.1

This working mechanism is confirmed by more fundamental studies for the mechanistic movement of F_1 motor of ATP synthase (Adachi et al., 2000; Al-Shawi and Nakamoto, 1997; Noji et al., 1997; Wang and Oster, 1998). As ATP

interacts with the three catalytic sites (cyclic sequence of binding, hydrolysis, and product release) that are located at the αβ interface (one on each β-subunit), the conformational changes in the helical loop within the β-subunits promote the hinge-bending motion of the β-subunit, and this bending motion pushes the γ-subunit. This way, a rotary torque is generated by the geometric propagation of elastic strain. This rotation is counterclockwise in discrete 120° steps when viewed from the F_o side. The driving torque is exerted on the γ-subunit by the β-subunits, which means the β-subunits push the γ-subunit periodically. Thus, this is the push motion for the rotation of the γ-subunit. The helical loop within the β-subunits is the asymmetrical packing segment in terms of the segmental analysis shown in Figure 14-4(j). The study by Wang and Oster (1998) also indicates that the other forces including electrostatic and steric ones are involved in the generation of the push motion, which may be interpreted as at least two element forces combining to produce this particular push motion. Steric force is solely repulsive, but this electrostatic force can be either attractive or repulsive. Hence, if the electrostatic force is repulsive, two element forces are involved. If it is attractive, three element forces are combined. The γ-subunit is always attached on (complexed with) the $\alpha_3\beta_3$ hexamer. This can be viewed as that the direction of the push motions (the rotation; not the counterclockwise one, which can be changed depending on the conditions) is inherited by the morphology of the single building unit, the ATP synthase. This is the logic that the guide motion is not defined here. The whole movement is triggered when the external signal (ATP) is recognized by (bound on) the three catalytic sites; therefore, these catalytic sites are the external force–specific functional segment. Nonetheless, the rotation of the γ-subunit is generated through periodic repetition of push motions, that is, type I working mechanism. As far as there is a critical role of the asymmetric packing segment (helical structure) in the mechanical movements and they are triggered by the ATP-binding energy, the working mechanism of this ATP synthase–based nanodevice may look similar to the kinesin-based one shown in Figure 14-9(a). However, the element motions that are generated by them are different despite the similarities in their segmental structures. Unlike the ATP synthase, kinesin is separated from (not complexed with) its partner protein, microtubule. This simple structural innovation works perfectly for the generation of a unique directional motion of kinesin through its APT-dependent conformational changes and logical contact with the microtubule. This may serve as another great example that shows the superior effectiveness and efficiency of nature's assembly strategies when designing nanosystems. It has been shown (Wang and Oster, 1998) that the efficiency of the F_1 motor was almost 100%.

The second nanodevice is a fullerene-based nanocar. The fullerene-wheeled building unit from Figure 14-4(a) is placed on gold surface. A thermal energy that can induce surface diffusion of this building unit triggers its movement on gold surface. Furthermore, because of the molecular configuration of the fullerene-wheeled building unit, its movement is favored in a certain direction. It is confirmed that this is through a rolling of the four fullerene molecules and not through a simple sliding

(for full details, see Shirai, 2006). It thus can be viewed that periodic push motions to the fullerene-wheeled building unit operate this nanodevice. Unlike the first nanodevice in this figure, this nanodevice works without an external force–specific functional segment.

The third one is a nanooscillator. This is purely a conceptual design. No actual building units for this nanodevice are presented in Figure 14-4. On solid substrate, two self-assembly building units having, for example, magnetic property, are fabricated at both ends of it. A selective attachment of the third building unit, for example, a fabrication building unit also having magnetic property, at the center of the substrate completes the fabrication of this nanodevice. The operation can be induced by inducing alternative periodic push motions between the self-assembly building units and the fabrication building unit, which can result in oscillation of the fabrication building unit. The reason that the building unit at the center has to be a fabrication building unit is that the proper modification of its surface (or a part of it) with a rigid organic or biological building unit can increase the success rate of the correct positioning of it during fabrication. A self-assembly building unit assembled with another self-assembly building unit for further assembly makes a fabrication building unit (for more details, see Subsection 2.2.2). For this nanodevice, both self-assembly and fabrication building units have an external force–specific functional segment that is sensitive on external magnetic field. A report about thermally induced rotation of surface-bound single molecules provides some valuable insight into this conceptual design (Baber et al., 2008).

14.3.5. Periodic Pull Motions

Figure 14-6 presents nanodevices that show periodic pull motions of the working mechanism. The first one is a nanomotor. A single-walled carbon nanotube is attached in the middle of solid substrate. Then, a metal pedal is attached on top of this carbon nanotube. Attaching the third building units around the metal pedal completes the fabrication. As with the previous nanodevice for type I in Figure 14-5(c), this is purely a conceptual design. The metal pedal attached on top of the carbon nanotube has to be free of rotation. This can ensure that, when alternating magnetic field is imposed on the building units around it, this metal pedal can be pulled by them also in an alternative manner. This can result in the constant rotation of the metal pedal through consecutive magnetic attractions between the two building units. Intrinsic magnetism of the building units is their external force–specific functional segment.

The next nanodevice is a two-way nanoswitch. The structure and fabrication are almost the same as for the one shown in Figure 14-5(c). One difference is in the fabrication building unit in the middle of the substrate. The substrate and the two building units at both ends of it are connected through a circuit. This nanodevice operates through the pull motion of the fabrication building unit by the building units at both ends. Alternative pull motions between the two building units through either electric field or magnetic field can alternatively connect two out of the three points in the circuit. Both building units should have an external force–specific functional segment. This is also a conceptual design.

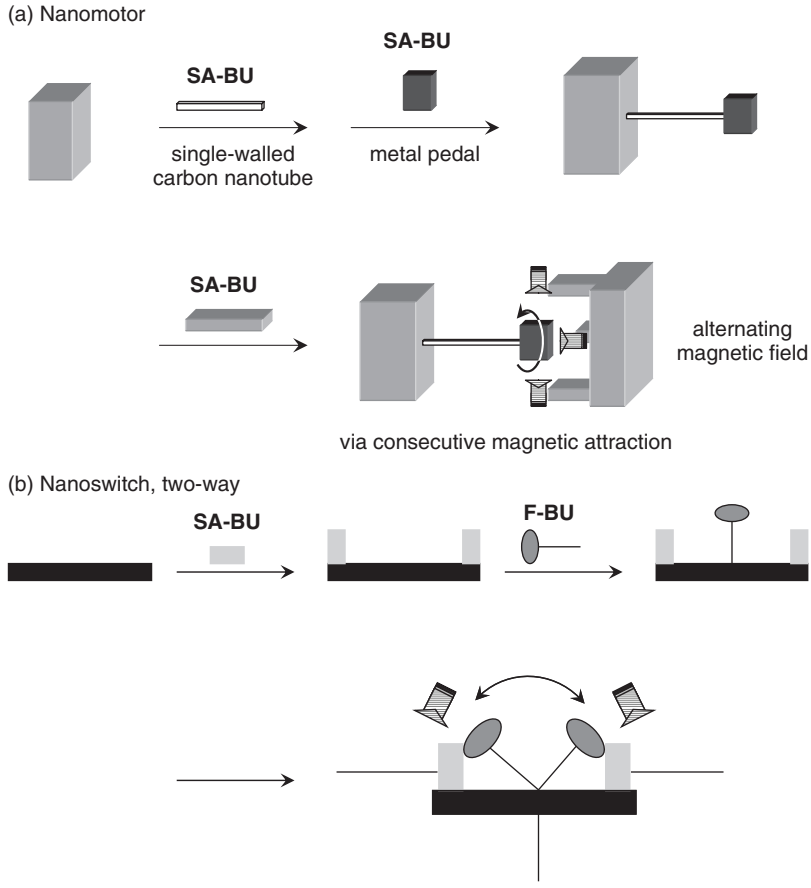


Figure 14-6. Nanodevices that show periodic pull motions (type II) of the working mechanism. **SA-BU** and **F-BU** refer to self-assembly and fabrication building units, respectively.

14.3.6. Push–Pull Motion Cycles

Figure 14-7 presents nanodevices that show push–pull motion cycles of the working mechanism. The first one is a nanogate. ω-(triethoxysilyl) alkanoic acid is fabricated on both edges of silica nanopore. This could be performed through the silylation of triethoxysilyl groups of ω-(triethoxysilyl) alkanoic acid with silica. One of the dyes from Figure 14-4(b) is then placed with it. The carboxylic group of ω-(triethoxysilyl) alkanoic acid is its directional segment. However, in this particular situation, it can perform the role of external force–specific functional segment as well by responding to solution pH. By properly changing the solution pH, hydrogen bonding can be induced between the carboxylic groups from both edges of silica nanopore. This generates a pull motion between them so that they can close the gate. This either retains the dye molecule inside the nanopore or keeps it outside of the nanopore. The solution pH also can be adjusted in a way to induce

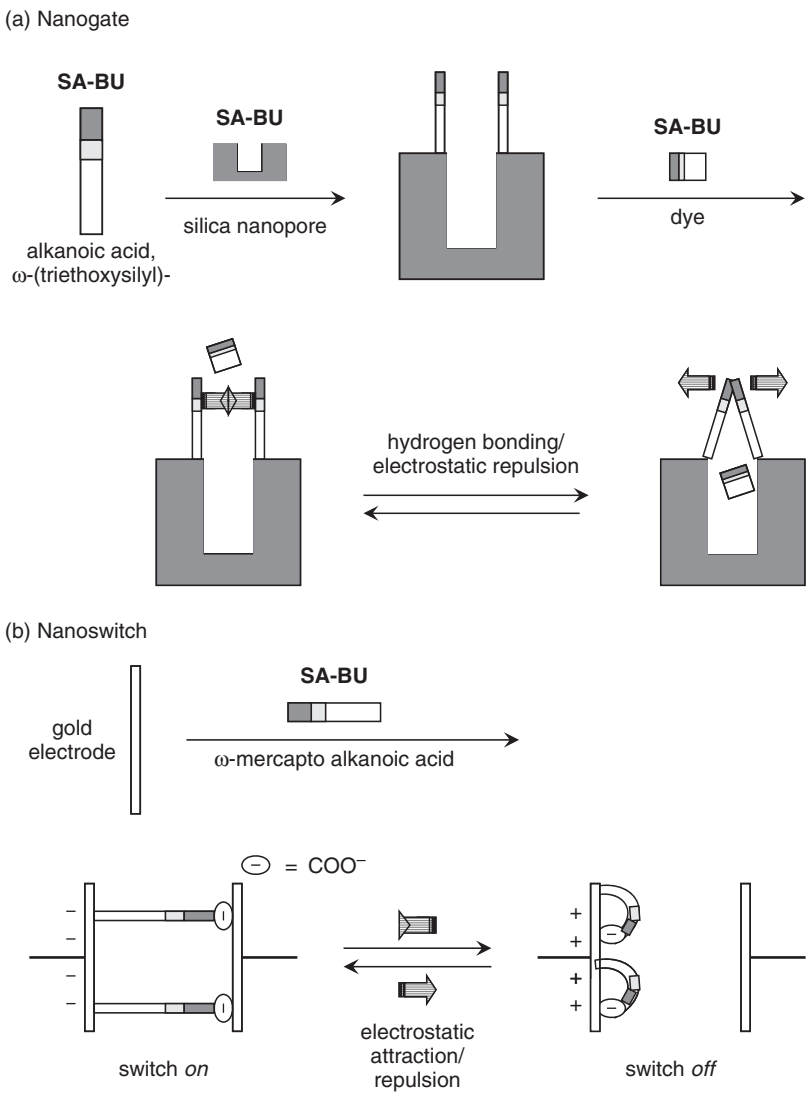


Figure 14-7. Nanodevices that show push–pull motion cycles (type III) of the working mechanism. **SA-BU** refers to self-assembly building unit.

an electrostatic repulsion between the two carboxylic groups. This can generate a push motion between them, which opens the gate. The dye molecule can now go through the nanopore, either by diffusion or by controlled assembly. As long as the structural integrity of this nanogate is maintained (especially the silanized part), the cycle of push–pull motions can be repeated. This is a conceptual design. The proof-of-concept of this nanogate was shown by Casasús et al. (2004) using amine-based trimethoxysilyl building units. A self-oscillating gel actuator that was assembled

with *N*-isopropylacrylamide-based copolymer shows a related actual example of a cycle of push–pull motions that is responding to a chemical wave (Maeda et al., 2008).

Nanoswitch is the next one. Gold substrate is used as an electrode. ω-mercapto alkanoic acid from Figure 14-4(a) then functionally self-assembles on the surface of the gold electrode. "Functionally" here means that both of the building units have to be located with enough space between them so that they can ensure a proper switching function. As with ω-(triethoxysilyl) alkanoic acid, ω-mercapto alkanoic acid has attractive and directional segments, and the directional segment (carboxylic group) can work as an external force–specific functional segment by responding to electric current. When the carboxylic group is fully ionized and thus becomes negatively charged, and if the gold electrode is also negatively charged, then ω-mercapto alkanoic acids with a long enough hydrocarbon chain can be pushed away from the gold electrode through an electrostatic repulsion. This can turn the nanoswitch *on*. The second gold substrate should be fabricated within the right distance. This geometrically controlled fabrication is the key to successful operation of this nanodevice. Moreover, it is known that ω-mercapto alkanoic acids with long hydrocarbon chains have the capability to conduct an electric current. When the electric current on the first gold electrode is changed into positive, it attracts the carboxylic group through a pull motion through an electrostatic attraction. The nanoswitch is then turned *off*. As long as the structural stability of the self-assembled monolayers of ω-mercapto alkanoic acids on gold surface is maintained, the repetition of this pull–push motion cycle can ensure the continuous operation of this nanodevice. There is an article (Mendes, 2008) that reviews the proof-of-concept, different examples, and the potential applications of this type of nanodevice. Details about the reversible transitions between straight and bent conformations of ω-mercapto alkanoic acid in response to an electric potential can be found in Lahann et al. (2003).

Case Study 14.2

The operation mechanism of the altitudinal molecular rotor that is fabricated on the surface of gold (Mulcahy et al., 2009) provides a good actual example of this type of nanodevice. The rotator for this system is the phenanthrene-based structures in the middle of the rotor, and the stators are the two cyclobutadiene rings that are attached with four phenyl groups. Their experimental results from IR spectroscopy strongly suggest that the cooperative combination of the three intermolecular forces generates the consecutive push and pull motions on the rotator, thus rotating it. The electrostatic force is exerted on the rotator by the gold surface, and there are H–H repulsion and π-conjugation force between the stators and rotator. There is no need to define the guide motion since the direction of the rotation is inherent here. The authors studied the generic rotation of the rotator, and did not change any external conditions that could affect the rotation. However, all three intermolecular forces could be varied in response to simple external forces, for example, thermal energy, which would accordingly change the direction and speed of the rotation. In this sense, it

would be reasonable to see the phenanthrene-based rotator itself as the external force–specific functional segment for this system.

14.3.7. Periodic Push Motions under Guide Motion

Figure 14-8 has the nanodevices that show this working mechanism. The first one is a rotaxane-based nanoshuttle. Two building units from Figure 14-4(g) are fabricated with solid substrates. The two tri(isopropyl)silane groups at both ends of the linear-shaped building unit can be attached on two separate silica substrates through silylation. The ring-shaped building unit has to be placed in the middle of the linear-shaped one during this fabrication. Once fabricated with the proper geometry, an electrostatic repulsion can be generated between the external force–specific functional segments of the ring-shaped building unit and the benzene rings from the linear-shaped building unit. This is possible through a controlled change in solution condition. Its alternating change can promote alternating repulsion, which is a periodic repetition of push motions. This push motion is always exerted along the direction of the linear-shaped building unit because of its geometrical confinement. This is a guide motion for this nanodevice. Hence, this is a nanodevice with a type IV working mechanism. For more details about rotaxane-based nanodevices, refer to the literature (Anelli et al., 1991). For full information about nanodevices from Stoddart's group, many of their review papers are valuable to read including Northrop et al., (2007). Another article (Balzani et al., 2002) clearly explains the perspective of force balance in the operation of nanodevices based on pseudorotaxanes. The nanodevice shown here is a schematic one based on the principles from that article.

The catenane-based rotary molecular motor (or single rotor) is the next one. The two building units from Figure 14-4(h) are fabricated to be interconnected to each other. This is the case when a well-designed synthetic route is required for the fabrication of nanodevice. A properly controlled solution condition can promote an electrostatic repulsion between the external force–specific functional segments of both building units in a stepwise manner. One-by-one push motions can generate the rotation of the small ring-shaped building unit along the direction of the large ring-shaped one. This can be viewed as a periodic repetition of push motions under a guide motion. This is a schematic one. Its proof-of-principle was demonstrated with somewhat different types of building units (Hernández et al., 2004; Leigh et al., 2003).

The third nanodevice is a purely conceptual design. Its proof-of-principle has not been reported. This is an azobenzene group–powered nanospring (or nanopiston). The function of the external force–specific functional segment of the azobenzene-based building unit was shown in Figure 9-3. It is assumed here that a similar azobenzene-based molecule has both ends functionalized with a reactive attractive group. Thus, this is a fabrication building unit. The second fabrication building unit is the one where one end can be attached to both ends of the azobenzene-based building unit. (Notice that this step of fabrication is especially conceptual.) This is then assembled with anodic alumina nanochannel from Figure 14-4(f) in such a

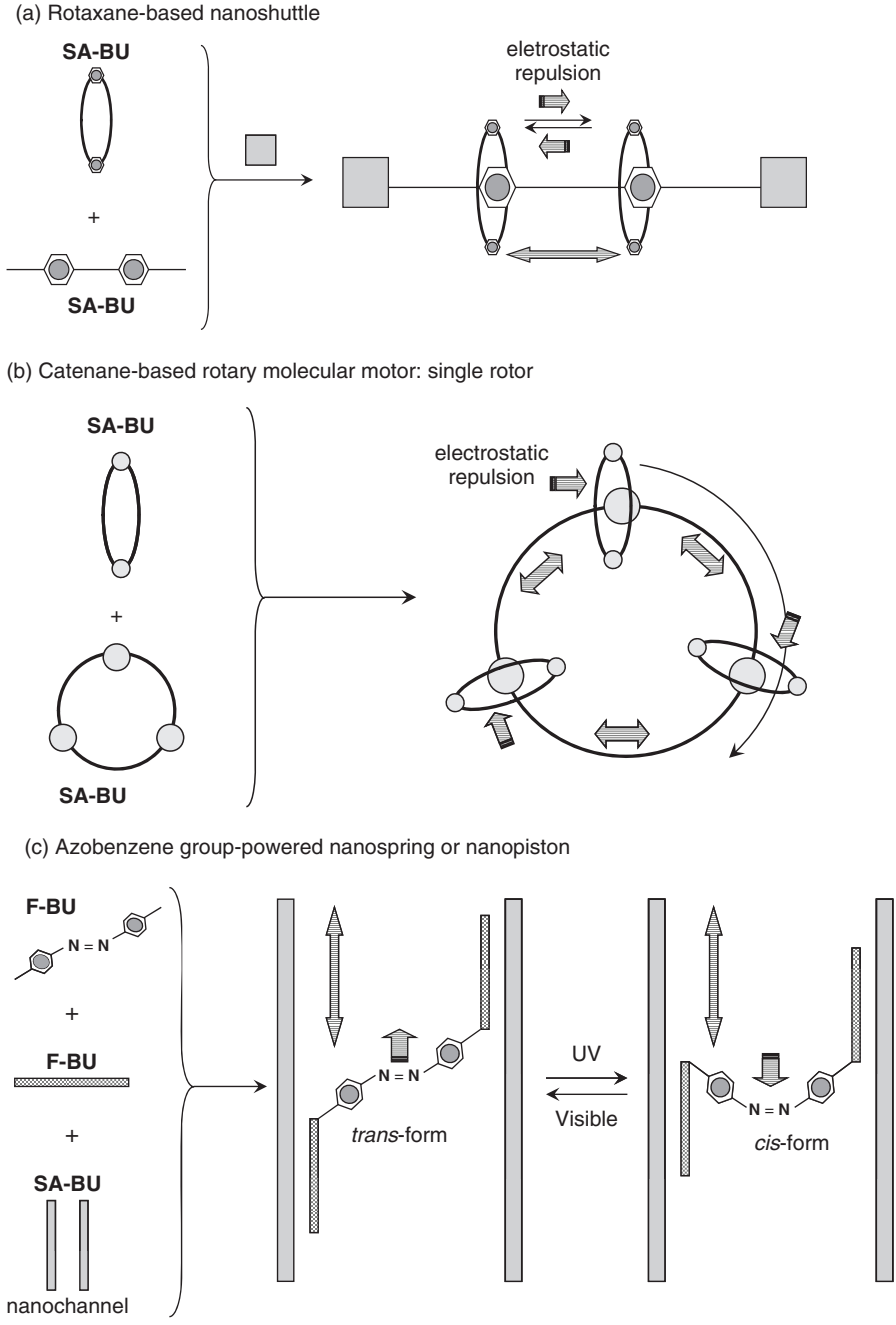


Figure 14-8. Nanodevices that show periodic push motions under guide motion (type IV) of the working mechanism. **SA-BU** and **F-BU** refer to self-assembly and fabrication building units, respectively.

way that the two building units are placed within the nanochannel. The azobenzene group is the external force–specific functional segment for this nanodevice. When ultraviolet light is irradiated, the azobenzene segment is converted into *cis*-form. When it is switched to visible light, this segment changes its position into *trans*-form. Each of these positional changes can be viewed as a push motion powered by the azobenzene group, which can provide a periodic spring-like (or contraction-and-expansion-like) or piston-like movement of the rod-shaped second building unit. The alumina nanochannel drives the direction of this movement. This is a guide motion of this nanodevice.

14.3.8. Periodic Pull Motions under Guide Motion

Figure 14-9 presents the nanodevices that show this working mechanism. The first one is a motor protein–based nanocargo. Gold nanoparticle is attached on top of the kinesin shown in Figure 14-4(i). In a separate step, microtubule shown in the same figure is fabricated between two solid substrates. The fabricated kinesin and microtubule are assembled in a way that kinesin is placed on top of microtubule. By exerting a proper ATPase cycle, it is possible to induce a directional walking-type of movement of kinesin on top of microtubule. This is performed via one-by-one pull motions to each external force–specific functional segment of the two kinesin "legs" by the external force–specific functional segment of microtubule. It thus is a periodic repetition of pull motions. And the direction of the long axis of microtubule is the direction of cargo movement, which is the guide motion for this nanodevice.

Case Study 14.3

A group of recent studies (Peterman et al., 2001; 2004; Rice et al., 1999; Sosa et al., 2001) provided strong visual and quantitative evidence that there is a directional ATP-driven chemomechanical cyclic movement of kinesin on the surface of microtubule. And it generated a stepping event with 8 nm intervals. Furthermore, they clearly revealed that the cyclic stepping event of a dimeric kinesin motor was the result of a cyclic repetition of the mechanical motion where kinesin heads are pulled by the binding site on microtubule, which is a periodic repetition of pull motions. Since these pull motions are induced by microtubule, their motion is always along the direction of microtubule. This is the guide motion. Therefore, this belongs to the type V working mechanism, which is a periodic repetition of pull motions under a guide motion. The authors claimed that the electrostatic interaction plays an important role in this processivity and directionality. They also showed that the conformational changes associated with this movement are greatly controlled by the changes in the structures of α-helix parts combined with the changes in the intermolecular forces within kinesin and microtubule and between them. The α-helix parts can be viewed as their asymmetric packing segment. Also, this is an APT-driven process; thus the part that is susceptible to APT is the external force–specific functional segment. The

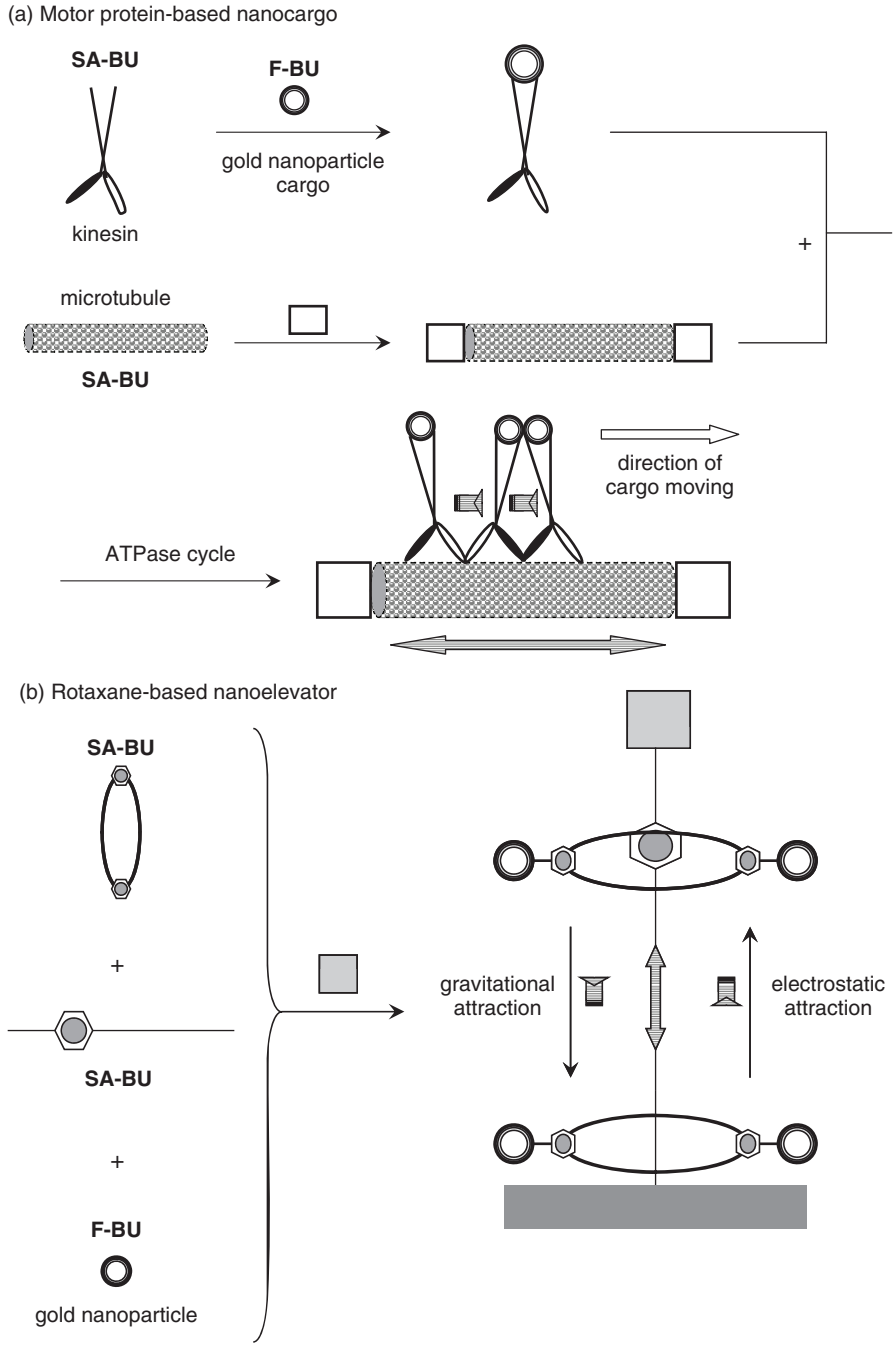


Figure 14-9. Nanodevices that show periodic pull motions under guide motion (type V) of the working mechanism. **SA-BU** and **F-BU** refer to self-assembly and fabrication building units, respectively.

attractive, repulsive, and directional segments cannot be specified here. However, the results strongly indicate that the two motions are generated as a result of the interplay and balance among all these intermolecular forces. Nature made a rational combination of those forces to come up with elegant and highly functional mechanical motions within biological cells. The authors also showed that the incorporation of additional segments and the changes in the environmental conditions strongly alter the processivity of kinesin, which is mostly likely induced by the changes in electrostatic interactions. This, too, could be traced with the view of three element motions if there were enough experimental and structural results.

Case Study 14.4

A directed treadmill motion of the bacterial actin MreB monomers on MreB filaments *in vivo* was revealed (Kim et al., 2006). This study also provides a strong indication that the treadmill motion is the result of the cyclic pull motions under the control of guide motion. A segment of the monomer is pulled by the binding site of the filament and the filament itself directs the whole movement. As with kinesin, helical structures seem to play a critical role, thereby becoming an asymmetric packing segment for this system. The part that is susceptible to the *in vivo* chemical signal is the external force–specific functional segment. Hence, this becomes another good example of a type V working mechanism.

Besides these specific cases, there is also an emerging theme that one key to understanding general self-assembly and disassembly processes within biological cells, which in turn often changes the overall biochemical cellular activity, is the balance among all the intermolecular forces involved (Chicurel et al., 1998). It is interesting to read the Chicurel et al. article with the notion of the asymmetric packing segment and the role of external force on the overall force balance combined with the symmetric balance between attractive and repulsive segments.

Figure 14-8(a) showed a rotaxane-based nanoshuttle. For the second nanodevice of type V, a conceptual rotaxane-based nanoelevator is shown. The ring-shaped building unit is the one shown in Figure 14-4(g). However, the second building unit is a linear-shaped rotaxane with only one benzene ring. Gold nanoparticle is a fabrication building unit. These three are spatially fabricated with solid substrate as shown in Figure 14-9(b). Once fabricated, it has to be placed in a vertical position relative to the direction of gravity. First, by controlling the solution condition with the ring-shaped building unit at the bottom, it can induce an electrostatic attraction between the two self-assembly building units, which could lift up the moving part. By controlling the solution condition back to where it was, it can eliminate this attraction. A gravitational force that is mainly exerted on the heavier gold nanoparticle pulls down the moving part to the original position. For this particular nanodevice, the weight of gold nanoparticle becomes its external force–specific functional segment. This is another expression of periodic repetition of pull motions. And its whole movement is directed along the long axis of the linear-shaped building unit, which is the guide motion of this nanodevice.

Case Study 14.5

A simulation study (Neild et al., 2009) that shows the possibility of double-walled carbon nanotube GHz oscillator can be a close real-world example. This particular system is composed of a core nanotube that slides back and forth within a fixed shell nanotube. Once the initial excitation force is applied to the core nanotube, periodically varying forces between the two nanotubes drive the oscillation motion. It is the van der Waals force that is responsible for this motion, and this oscillation continues until the damping force gradually stops it. van der Waals force is working between the core and shell nanotubes, but since the shell nanotube is fixed, it actually works as if it were exerted on the core nanotube by the shell nanotube by periodically changing its directions. Thus, it becomes the case that a single element force generates the pull motion, which is the same as for the one in Figure 14-9(b). One difference is that, for this nanotube oscillator, there is no need of continuous changing of the external force after the initial exertion of the excitation force. The core nanotube is a colloidal self-assembly building unit with an attractive segment only, as shown in Figure 14-4(c), but it can be analyzed as working as an external force–specific functional segment as well. The cyclic repetition of this pull motion is guided along the direction of the long axis of the shell nanotube. Thus, the guide motion is provided by the shell nanotube. Therefore, this double-walled carbon nanotube oscillator provides another example of a type V working mechanism. For the kinesin motor–based nanodevice, both pull and guide motions were generated through the combination of different element forces.

14.3.9. Push–Pull Motion Cycles under Guide Motion

Figure 14-10 has the nanodevices that show this working mechanism. The first one is a rotaxane-type DNA-powered nanomechanical sensor. This is a conceptual design. The two DNA building units from Figure 14-4(i) are fabricated with solid substrate and gold nanoparticle, respectively. The gold nanoparticle is pre-decorated with the proper dye molecule. These two then have to be fabricated in such a way that the ring-shaped building unit encircles them. The direction of the whole device has to be vertical relative to the direction of gravity. When the condition favors the release of the binding between the two DNAs, the DNA part attached with gold nanoparticle can move as if it were pushed away from the DNA part attached to solid substrate. When the condition is controlled back to having the two DNAs bind, they can move as if the one on the substrate pulls up the one with gold nanoparticle. It is a cycle of push–pull motions. The whole movement is performed along the direction of the long axis of DNAs. This is a guide motion. The displacement generated by this pull–push motion cycle could be used for sensing purposes. The design of logic gates based on the assembly of aptazymes and noncrosslinking gold nanoparticles (Ogawa and Maeda, 2009) demonstrates the potential of gold nanoparticles as a working part of nanodevices via combining with DNA–RNA complementarity. According to the terminology here, the aptazymes are a

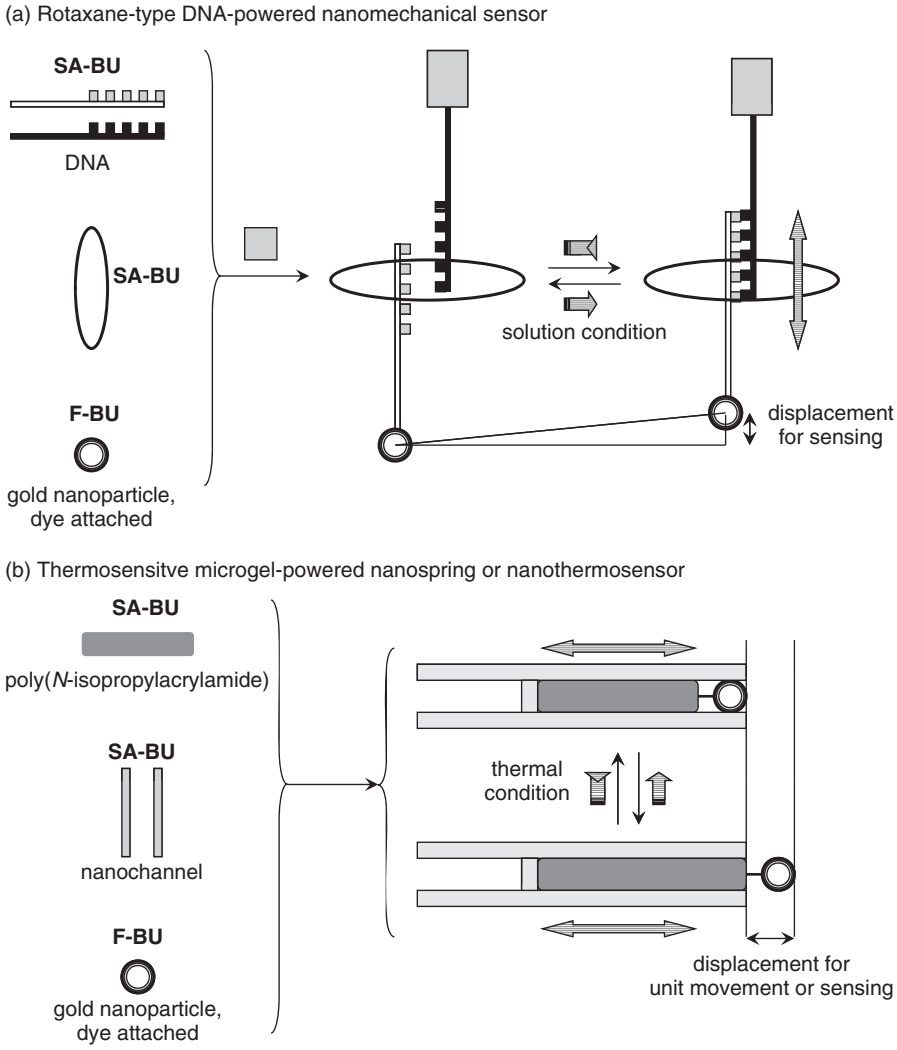


Figure 14-10. Nanodevices that show push–pull motion cycles under guide motion (type VI) of the working mechanism. **SA-BU** and **F-BU** refer to self-assembly and fabrication building units, respectively.

self-assembly building unit and the DNA-tethered gold nanoparticle is a fabrication building unit.

The next nanodevice is another conceptual design. It is a thermosensitive microgel–powered nanospring or nanothermosensor. The key building unit is the thermosensitive poly(*N*-isopropylacrylamide) from Figure 14-4(e). This building unit is fabricated inside the nanochannel of anodic alumina membrane. One end of poly(*N*-isopropylacrylamide) microgel is physically blocked while the other end is attached with gold nanoparticle. This gold nanoparticle has dye molecules

attached. As shown in Figure 9-8, the external force–specific functional segment of poly(*N*-isopropylacrylamide) microgel can trigger its reversible expansion and contraction as the temperature is controlled to go back and forth across the critical one. With a carefully designed geometry, when the microgel is expanded, it can work as if it pushes away the gold nanoparticle to the outside region of the nanochannel. When the microgel is contracted, it can work as if it pulls the gold nanoparticle back to its original position. This cycle of push–pull motions can be performed only along the direction of the nanochannel. This is a guide motion. The displacement prompted by the movement of the gold nanoparticle could be defined as a unit movement that corresponds to the absolute amount of microgel and the size of the nanochannel so that it could be used as a standard for more complicated nanoscale movements. It could be applied for sensing as well. If the mechanical movement of this nanodevice is particularly emphasized, its stable reversibility could make it useful as nanoscale machinery, such as a nanoscale spring.

14.3.10. General Trends

Nanodevices can be fabricated with huge diversity and complexity. Figure 14-11 shows a general trend of the fabrication of nanodevices. Nanodevices with type

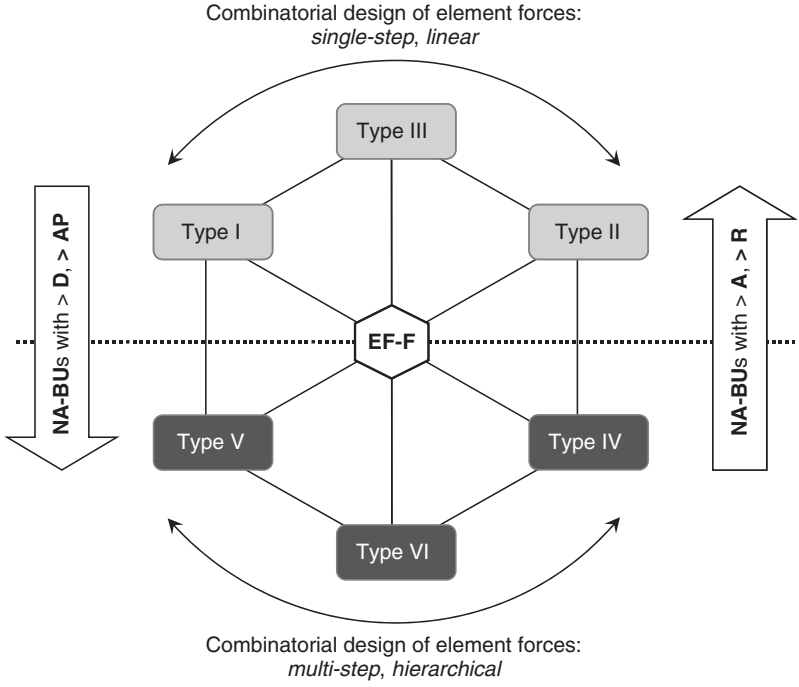


Figure 14-11. General trend of the design of nanodevices. **NA-BU** is short for nanoassembly building unit. **A, R, D, AP**, and **EF-F** refer to attractive, repulsive, directional, asymmetric packing, and external force–specific functional segments, respectively.

I, II, and III working mechanisms operate without the guide motion while nanodevices with type IV, V, and VI working mechanisms operate under the guide motion. This helps in selecting the building units—more specifically, the particular segments that should be included within the building units. The horizontal dot-line in the middle represents this. Generally, it is likely that nanodevices with type I, II, and III working mechanisms require more attractive and repulsive segments. And it is likely that nanodevices with type IV, V, and VI working mechanisms require more directional and asymmetric packing segments. This does not mean that nanodevices with type I, II, and III working mechanisms do not need directional and/or asymmetric packing segments at all. Likewise, this does not mean that nanodevices with type IV, V, and VI working mechanisms do not need attractive and repulsive segments. All four segments are important for all six types of nanodevices as long as they are rationally combined to express proper element motion(s). The combinatorial design of element forces is the key. For nanodevices with type I, II, and III working mechanisms, a few steps (or just a single step) of linear fabrication is often enough to achieve this. For nanodevices with type IV, V, and VI working mechanisms, multiple steps of hierarchical fabrication are usually necessary. For almost all nanodevices, the designing and positioning of the external force–specific functional segment are the very core steps in their fabrication because that is the only way (with a few exceptions) to ensure their proper functions in responding to external signals. Based on the absence/presence of the guide motion, type I nanodevices have a close link with type IV nanodevices. And type II and type III nanodevices have a close link with type V and type VI nanodevices, respectively. This means that type I and type IV nanodevices are likely to have common building units and similar responses to external signals. The same is true for type II and type V nanodevices, and type III and type VI nanodevices.

14.4. COLLECTION OF NANOMECHANICAL MOVEMENTS

Table 14-1 collects the nanomechanical movements that are reported in the literature. The types of nanosystems are determined based on the classification in Figure 14-3. Nanosystems that express different types of nanoproperties were shown in Tables 12-1, 12-2, and 12-3. These nanosystems were not unique for each nanoproperty. Different nanosystems often show the same nanoproperty. However, each of the nanosystems shown in Table 14-1 is unique, thus showing its own unique nanomechanical movement. By following the emphasis of each study, the mechano-motions shown here are more specific than those in the previous sections of this chapter. The same is true for the external signals for each nanosystem. Many studies report the specific direction of the movement, and express the degree of the movement by using duration time, moving distance, frequency, or velocity. These are also captured by following the emphasis in the literature. All of the nanosystems shown in this table are nanodevices. They all have the capability of nanomechanical movements, that is, unit operations. But none of them are actually integrated into nanomachines at this moment.

TABLE 14-1. Collection of different types of nanomechanical movements, nanosystems on which each mechano-motion is generated, its direction and degree, and external signals that trigger each movement.

Type	Nanosystem	Mechano-motion	Direction/Movement	External Signal
I	ATP synthase[1]	unidirectional rotation		ATP/ADP conversion
I	molecular motor consisted of triptycene and helicene units[2]	unidirectional rotation	$t_{1/2} \approx 5$ min	chemical energy
I	molecular motor consisted of chiral overcrowded alkenes[3]	unidirectional rotation		light
I	molecular rotor of hexa-*t*-butyl decacyclene on Cu surface[4]	molecular rotation		thermal
I	vesicle of didodecyldimethyl-ammonium bromide[5]	step-wise self-propulsion	linear with some randomness, $\sim\mu$m/min	anion exchange
I	nanomotors with asymmetric catalytic sites[6]	self-propulsion	linear with some randomness	chemical energy (catalysis)
II	double-walled carbon nanotube nanomechanical resonator[7]	oscillation		evaporated atom
II	multi-walled carbon nanotube-based torsional nanoactuator[8]	rotation	linear, MHz	electrostatic field
III	oligoheterocyclic strand with pyridine/pyrimidine units[9]	extension/contraction	linear, 3–5 nm	metal ion/pH
III	bacterial flagellar protofilament[10]	extension/contraction	linear, 0.08 nm	ATP/ADP conversion
III	crosslinked polypeptide[11]	extension/contraction	linear, up to mm	temperature, pressure, pH, light, chemical
III	molecular rotor consisted of phenanthrene and cyclobutadiene groups[12]	molecular rotation		generic
IV, V	various rotaxane-, catenane-, and pseudorotaxane-based nanodevices[13]	stepwise stepping/rotation	linear, circular	pH, light, chemical, electrochemical
IV	catalytic micropump: carboxylated polystyrene sphere[14]	periodic circle	$\sim\mu$m/s	decomposition of hydrogen peroxide

(*continued*)

TABLE 14-1. (*Continued*)

Type	Nanosystem	Mechano-motion	Direction/Movement	External Signal
IV	catalytic micropump: gold rod[14]	periodic circle	~μm/s	decomposition of hydrogen peroxide
IV	catalytic nanomotor: striped metallic nanorod[15]	linear	~μm/s	hydrogen peroxide/magnetic field
IV	dynein with microtubule[16]	directional translocation	~μm/s	ATP/ADP conversion
V	kinesin motor on surface of microtubule[17]	cyclic stepping	linear, 8 nm	ATP/ADP conversion
V	bacterial actin MreB monomer on MreB filament[18]	treadmill motion	linear	ATP/ADP conversion
V	double-walled carbon nanotube oscillator[19]	oscillation	linear, GHz	generic
V	myosin motor on actin filament[20]	cyclic stepping	linear, ~10 nm, ~μm/s	ATP/ADP conversion
VI	molecular automaton[21]			mRNA
VI	catalytic micropump: amidine-functionalized polystyrene sphere[14]	periodic circle	~μm/s	decomposition of hydrogen peroxide
unclear[a]	bacterial flagellar motor[22]	uni-(bi-)directional rotation	hundreds of Hz	transmembrane ion (H^+ or Na^+) gradient

[1] See Case Study 14.1 for more details.
[2] Kelly, 2001. In the sense that the trapping of the molecule in an energetically excited conformation can be viewed as that the rotor part is being pushed toward one direction, this is a type I mechanism.
[3] Feringa, 2001.
[4] Gimzewski et al., 1998.
[5] Miura et al., 2010.
[6] Paxton et al., 2006. Most of the examples in this review have a type I mechanism.
[7] Jensen et al., 2008.
[8] Yuzvinsky et al., 2006.
[9] Barboiu and Lehn, 2002.
[10] Samatey et al., 2001.
[11] Urry, 1993.
[12] See Case Study 14.2 for more details.
[13] For details about all the different types of nanodevices from Stoddart's group, please see Northrop et al., 2007 and the references therein.
[14] Kline et al., *J. Am. Chem. Soc*. 2005.
[15] Kline et al., *Angew. Chem. Int. Ed*. 2005.
[16] Numata et al., 2008.
[17] See Case Study 14.3 for more details.
[18] See Case Study 14.4 for more details.
[19] See Case Study 14.5 for more details.
[20] Bakewell and Nicolau, 2007.
[21] Benenson et al., 2004. The operation of this device is not based on a mechano-motion, but in the sense that it operates via logical binding and releasing of RNA-DNA complementarity along a predetermined direction, it could be viewed as a type VI mechanism.
[22] Thormann and Paulick, 2010.
[a] Exact mechano-mechanism has not been determined. But based on their geometrical characteristics, it could be either type I, II, or III.

14.5. SUMMARY

This chapter showed how to design nanofabrication for a specific nanodevice and the fundamental principles for the generation of nanomechanical movements. It further showed that:

1. Nanodevices can be effectively fabricated when the principles of self-assembly are rationally designed during nanofabrication.
2. Nanomechanical movements of each nanodevice are generated by the cooperative interactions of the three element motions.
3. The three element motions are generated by the cooperative interaction of the five element forces.
4. Based on these factors, the working mechanisms of nanodevices are classified into six representative types.

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16

Assembly Processes and Critical Behaviors

16.1. CRITICAL BEHAVIORS AS THE CHARACTERIZATION GUIDE OF ASSEMBLY PROCESSES

Critical behaviors (or *critical phenomena*) are typically defined as unusual changes of physical properties at critical points. And *critical points* (or *critical states*) are defined as the points of any condition where a phase boundary begins to become unclear. For self-assembly processes, the best-studied, both experimentally and theoretically, critical behavior is the critical micellar concentration (*cmc*). At the point (a narrow range of concentration, to be exact) of critical micellar concentration, the monomeric solution of amphiphilic molecules begins to be transformed into a micellar solution. The monomeric solution is a homogeneous solution of amphiphilic molecules, which makes it a single monomeric phase. The micellar solution, on the other hand, is composed of a certain concentration of monomers with newly formed micelles. Physically, these micelles can be viewed as another phase within the micellar solution. (The term *pseudo-phase separation* comes from this view.) When the concentration of amphiphilic molecules is decreased below the critical micellar concentration, the micellar solution changes back into a single-phase monomeric solution. It thus justifies the "critical" within the term *critical micellar concentration*. The amphiphilic molecules have diverse origins, including surfactants, bio-mimetic molecules, biological molecules, and a certain type of polymer.

When micelles are formed at the critical micellar concentration, the physical properties as well as many other properties of the micellar solution are changed in

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TABLE 16-1. Collection of physical properties to measure for the characterization of critical behaviors during assembly processes. m, c, b, and b-m refer to molecular, colloidal, biological, and bio-mimetic assembly processes, respectively. p indicates that the property is mainly useful for primary assembly processes. h indicates that it can be useful for both primary and higher-order (hierarchical) assembly processes.

Property	Assembly Process	Type of Change at Critical Point	Assembly Order
surface tension	m, b, b-m	abrupt	h
interfacial tension	m, b, b-m	abrupt	h
contact angle	m, b, b-m	gradual	p
wetting, dewetting	m, b, b-m	transitional	p
electrowetting	m, b, b-m	transitional	p
capillarity	m, b, b-m	gradual	h
sliding	m, b, b-m	transitional	p
spreading	m, b, b-m	transitional	p
bridging	m, b, b-m	transitional	p
diffusion	m, c, b, b-m	abrupt	h
surface diffusion	m, c, b, b-m	abtrupt	h
turbidity	m	abrupt	p
spectral intensity	m, c, b, b-m	stepwise	h
viscosity	m, b, b-m	gradual	h
conductivity	m, b, b-m	abrupt	h
pH	m, b, b-m	stepwise/transitional	h
flow	m, c, b, b-m	gradual	h
phase inversion	m	transitional	p
phase transition	m, b, b-m	transitional	h
clouding	m	abrupt	p
hydration	m, b, b-m	abrupt	p
crystallization	m, c	gradual	p
precipitation	m, c	gradual	p
zeta potential	c	gradual	h
direct imaging	c	gradual	h

an unusual manner, often dramatically. More generally, when a critical behavior is observed for a certain assembly system, it is usually a strong indication that the assembly system is undergoing dramatic physical changes by forming self-assembled aggregates. This in turn suggests that measuring the unique physical property for each assembly system can provide a practical way to identify its capability for self-assembly. In addition, by tracking the changes in the physical properties, it is possible to characterize the processes of the assembly. The proper interpretation of the changes and the degree of the changes can provide detailed process information (for the collection of physical properties, refer to Table 16-1). Thus, critical behaviors can be not only one of the key indicators that there is an assembly process taking place (Lindman, 2002), but a facile guide to fully characterizing whole assembly processes as well.

It is rare for a self-assembly to take place without going through any critical changes in physical properties. And critical behaviors occur during assembly processes with multiple building units, too (for assemblies with multiple building units, refer to Chapter 7). The pattern of changes can be different depending on the assembly modes (for more about the assembly modes, see Figure 7-1). For all-at-once

assemblies, there is only one critical change. For successive assemblies, there are two or more critical changes with a similar pattern. For sequential assemblies, there are two or more critical changes but with different patterns. Hierarchical assemblies also show two or more critical changes, but the patterns can be similar or different depending on the building units. Critical behaviors for assembly processes can be observed both in solution and at surface. Usually the critical changes are more dramatic in solution than at surface, but this is not absolute. Some assembly systems show more dramatic changes at surface than in solution, especially when solubility of the building units is low but they have high adsorption and assembly affinity on the surface. Critical behaviors are also observed during directed and forced assembly processes (for more about these assemblies, see Chapter 8). For these processes, it is usually the external forces themselves that are critically changed during the assembly. For assemblies that are responsive to external signals (for more about these assemblies, see Chapter 9), what is changed is not the external signals that are imposed on the assembly systems but the physical properties that are used to trace the changes during the assembly processes. Thus, critical behaviors can be used as a key guide to characterize the assembly processes not only for self-assembly but for a broader range of nanoassembly as well (for details on self-assembly and nanoassembly, and their relationships, refer to Section 2.6). The characterization principles shown in the next section are based on characterization of the critical behaviors of each assembly system.

16.2. CHARACTERIZATION PRINCIPLES

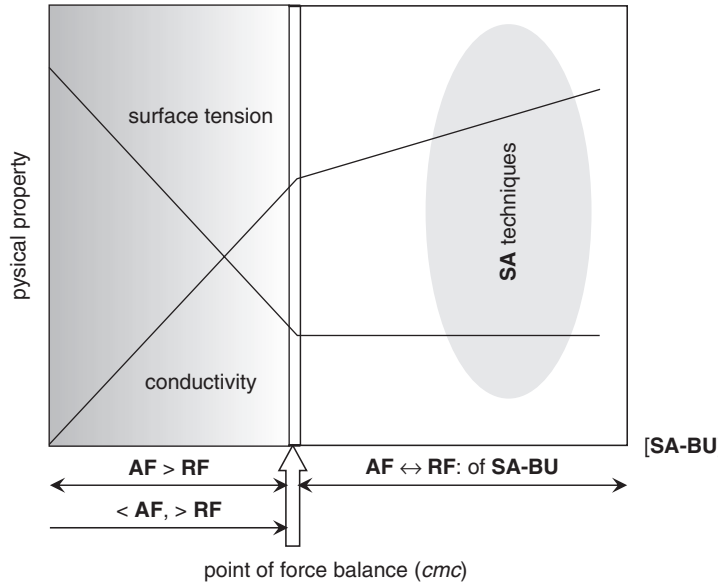
Section 15.5 showed how the structural information of assembly building units could aid in the selection of characterization techniques for their assembly processes and assembled systems. The figure does not pinpoint the exact techniques for each assembly system, but it can make the characterization quite efficient by narrowing down the most practical techniques. This section shows how the assembly processes of different systems can be characterized based on this approach. It does not cover the full scope of experimental techniques available, but shows how the concept of segmental analysis can contribute to actual experiments (for more about *segmental analysis*, see Subsection 1.2.2).

16.2.1. Self-Assembly Capability

Figure 16-1 is an experimental guide to how assembly capability can be characterized. This general guide is valid for assemblies both in solution and at surface.

16.2.1.1. Molecular Systems. Figure 16-1(a) is for building units of a molecular nature. It includes bio-mimetic and biological building units as well. The horizontal axis represents the concentration of the building units. The concentration is increased as it goes to the right-hand side. The vertical axis represents the physical properties that are sensitive on the changes in the concentration of the

(a) Molecular, bio-mimetic, and biological **SA-BU**s



(b) Colloidal **SA-BU**s

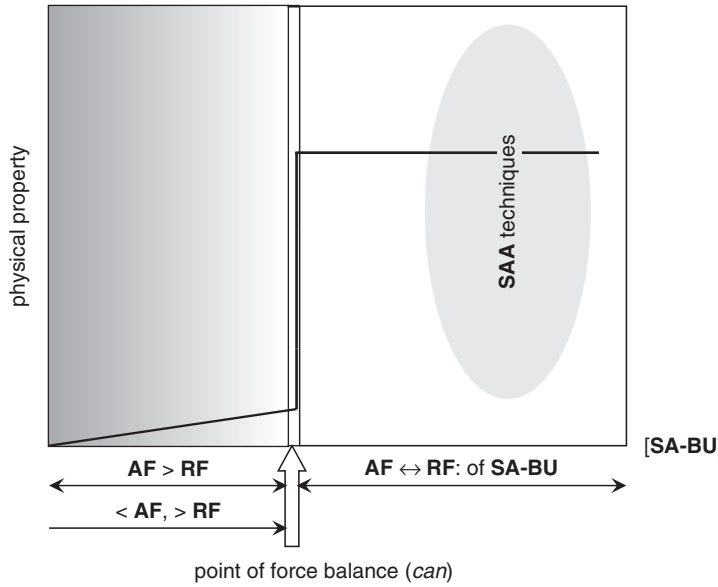


Figure 16-1. Experimental guide for the characterization of self-assembly capability. **SA-BU** is short for self-assembly building unit. **SA** and **SAA** are short for self-assembly and self-assembled aggregate, respectively. **AF** and **RF** refer to attractive and repulsive forces, respectively. *cmc* and *can* are critical micellar concentration and critical aggregation number, respectively.

building units. Since this is for molecular building units, the point of force balance between them where the assembly process begins to take place (for details about this concept, see Section 3.3) becomes the critical micellar concentration (*cmc*). After the *cmc*, the attractive and repulsive forces between the building units remain balanced. Before the *cmc*, the attractive force is greater than the repulsive force, and the building units are in a monomeric state. The increase of the concentration can be viewed as if the attractive force were gradually decreased while the repulsive force is gradually increased. (The absolute magnitude of the attractive force keeps increasing. But its magnitude relative to the net sum of the attractive and repulsive forces keeps decreasing.) These two forces are balanced at the *cmc*.

To track the assembly processes experimentally, it is important to have a significant change in physical properties before and after the point of force balance. The point (a narrow range, to be exact) where this change occurs can be directly interpreted as the *cmc* of a particular assembly system. At the same time, the physical properties should be easy to measure. Two typical examples are shown in the figure. *Surface tension* is the degree of surface activity of a given liquid, and can be affected by the addition of the second component. Since most molecular building units are surface active, once they are placed in a liquid they decrease the surface activity of the liquid, thus reducing the surface tension. As the concentration of building units is increased, they keep reducing the surface tension until it reaches the point of force balance. At this point, the surface of the liquid is saturated by the building units, and the aggregates that begin to appear do not affect the degree of surface activity. Therefore, the surface tension tends to remain nearly the same. This was the bottom logic to have process techniques (**SA** techniques) shown in Figure 15-3. Another example is conductivity measurement. One difference is that the conductivity value is increased as the concentration of the building units is increased. The more building units in a liquid, the more ionized species are generated. After the point of force balance, the conductivity value levels off. The aggregates have the size of colloid; thus, a part of the ionized species is readsorbed on their surfaces. This makes the conductivity technique useful for characterization of ionic building units.

The **SA** techniques shown in Figure 15-3 are those that can be used to track the assembly processes. Depending on each assembly system, the actual variation pattern of the physical properties can be different. However, all of them can provide a clear change in the physical properties as a function of the concentration of the building units. This change shows an abrupt but unique break at the point of force balance, which confirms the assembly and provides assembly parameters. In other words, whenever the potential building units under consideration are molecular, and their segmental analysis suggests that they have the capability of self-assembly under a given condition, the mostly likely choice of experiments to confirm this is **SA** techniques. Nailing it down to one or two specific techniques is dependent on their availability and the assembly parameters that are required to be obtained.

16.2.1.2. Colloidal Systems. Figure 16-1(b) is for building units of a colloidal nature. Most building units whose sizes range from tens of nanometers to tens of

micrometers can be covered by this general guide. As with Figure 16-1(a), the horizontal axis represents the concentration of the building units. The vertical axis represents the physical properties. Before the point of force balance, the attractive force is greater than the repulsive force. As the concentration is increased (to the right-hand side), the attractive force is gradually decreased while the repulsive force is increased (the relative magnitude: see the first paragraph of Subsection 16.2.1.1 for more clarification). The concentration here is the number of colloidal particles per unit volume of solution (suspension, to be exact). Notice that this description for the change in each force is not what actually happens. At every point during the assembly process, the system reaches an equilibrium of its own. However, this analysis helps dissect the critical factors of the assembly process. Since this is for colloidal building units, the point of force balance becomes the critical aggregation number (*can*).

The uniqueness of following the colloidal assembly processes comes from their own properties. Colloidal building units are bigger than molecular ones. They stay in a dispersed form before the point of force balance. In most cases they are not surface active, or their surface activity is minimal, unless their surfaces are modified to be so. This makes them show minimal if any variation in changes in the physical properties being measured before the point of force balance. But the physical properties usually undergo a major change in responding to the formation of aggregates. Thus, most **SA** techniques are not useful for colloidal building units. On the other hand, the uniqueness of the colloidal building units brings the bottom logic for another group of techniques that can be practical for them. Their aggregates are big enough that they can be directly observed: not only their morphologies and sizes but the assembly processes as well *in situ*. This group of techniques is classified as structural techniques (**SAA** techniques) in Figure 15-3. The resolution can vary depending on each assembly system, and some of the techniques within this group can measure some important interaction parameters such as types of the forces and their strengths. Once segmental analysis of a certain colloidal building unit indicates that it has assembly capability, then it is most likely the **SAA** techniques that will confirm it. Surface **SAA** techniques (also in Figure 15-3) are useful for assemblies on surfaces while **SAA** techniques are usually practical for assemblies both in solution and at surface.

16.2.2. Multi-Step Self-Assemblies

The previous subsection showed that structural analysis of building units becomes useful when characterizing their assembly capability. Figure 16-2 is designed to show that the same is true for the characterization of multi-step assembly processes. This general guide works for assemblies both in solution and at surface.

16.2.2.1. Molecular Systems. Figure 16-2(a) is for molecular, bio-mimetic, and biological building units. The definition of each axis is similar to those in Figure 16-1. But the horizontal axis here also represents the amount of any additives

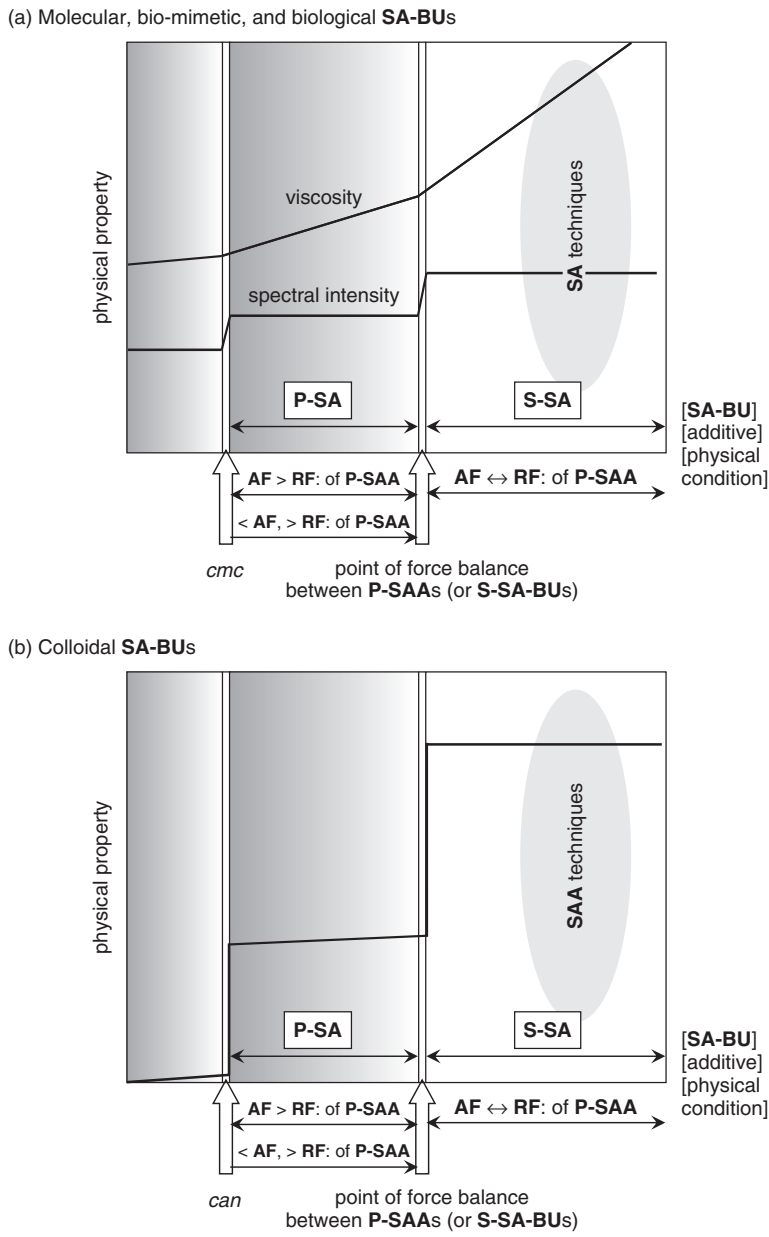


Figure 16-2. Experimental guide for the characterization of multi-step (hierarchical) self-assembly. **SA-BU** and **S-SA-BU** are short for self-assembly and secondary self-assembly building units, respectively. **SA** and **SAA** are short for self-assembly and self-assembled aggregate, respectively. **P-SA** and **S-SA** are short for primary and secondary self-assemblies, respectively. **P-SAA** is short for primary self-assembled aggregate. **AF** and **RF** refer to attractive and repulsive forces, respectively. *cmc* and *can* are critical micellar concentration and critical aggregation number, respectively.

and any physical conditions that have some degree of influence on the assembly processes. As the two typical examples shown in the figure indicate, most of the physical properties are measurable during the entire multi-step assembly process. The point of force balance is reflected by the point where there is a sudden change in the physical property. This is because the emergence of the aggregates in each step of assembly is on a much faster time scale than in most of the measuring techniques. And the techniques that are suitable for this are those that can show the most significant changes when the aggregates are formed, which are mostly **SA** techniques (shown in Figure 15-3).

The changes in the force balance between the building units are similar to those in Figure 16-1(a). The figure now has multiple steps. This figure considers up to the secondary processes. The formation of the primary aggregate is reflected by the critical micellar concentration (*cmc*). After this first force balance, the attractive force between the primary aggregates (or the secondary building units) remains greater than the repulsive force between them until the assembly reaches the point of the next force balance. But as the concentration of any (or all) of the substances at the horizontal axis is increased, the amount of the primary aggregates is gradually increased. This promotes the gradual increasing of the repulsive force between them while the attractive force gradually decreases. (The absolute magnitude of the attractive force between the primary aggregates keeps increasing. But its magnitude relative to the net sum of the attractive and repulsive forces keeps decreasing.) The point of force balance between the primary aggregates is reflected by a sudden change in physical properties. For many molecular building units, this point is called the *second cmc*. The secondary aggregates begin to form at this second *cmc*. After the second *cmc*, the attractive and repulsive forces between the primary aggregates (within the secondary aggregates) remain balanced until the secondary aggregates reach the point of another force balance if there is any.

16.2.2.2. Colloidal Systems. Figure 16-2(b) is for colloidal building units. Both axes have the same definition as for Figure 16-2(a). The horizontal axis represents the concentration of colloidal building units. It is also for the amounts of any additives and the degree of any physical conditions. The vertical axis is for the physical properties that are measured to track the assembly processes. The bold line inside the figure shows the most likely change in the physical properties as the colloidal particles assemble. In contrast to the molecular assemblies whose physical properties change with some degree of continuity, the change here is dramatically stepwise. And as discussed in Figure 16-1(b), the changes before the first force balance (*can*: critical aggregation number) are minimal or negligible in almost all cases. A part of the reason is that there is the possibility of forming pre-aggregates (aggregates that are formed well below the force balance point with much lower aggregation numbers than the one at the point of the force balance). For colloidal particles, this tends to occur at much lower concentration than for molecular building units. After the first force balance, the physical properties suddenly become

measurable. Usually, the physical properties are changed a little during the primary assembly processes. This is mainly because the physical properties that are measured are mostly the direct imaging. As the assembly continues, the primary aggregates (secondary building units) that are formed at the *can* reach the point of the second force balance. This is called the *second can*. At this point of the second force balance, the physical properties make another big jump, and are changed a little during the secondary assembly processes. The **SAA** techniques are suitable for tracking these processes (Figure 15-3). A specific technique can be chosen from among them based on other experimental information that may be required for each assembly system.

Figure 16-1(b) explained the changes in the force balance between the colloidal particles up to the first force balance. After this first *can*, whenever the conditions are favorable, the colloidal particles go into secondary assembly processes. For the primary aggregates that are formed at the first *can*, the attractive force between them is greater than the repulsive force and stays this way until they reach the point of the second force balance. As the concentration of colloidal particles or any other favorable parameter on the horizontal axis is increased, the number of primary aggregates gradually increases as well. This promotes the gradual increasing of the repulsive force between them while the attractive force gradually decreases (the relative magnitude: see the second paragraph of Subsection 16.2.2.1 for more clarification) until the process reaches the point of another force balance. This is the second *can*. The attractive and repulsive forces between the primary aggregates (within the secondary aggregates) remain balanced until the secondary aggregates reach the point of another force balance if there is any.

16.3. COLLECTION OF PHYSICAL PROPERTIES TO MEASURE

Table 16-1 collects the physical properties to measure for the characterization of critical behaviors that occur during assembly processes. These are the ones that appear frequently in the literature. The types of assembly processes that are suitable for each physical property are also shown. But note that this indicates the general aspect of each physical property, and is not an absolute condition. The same is true for the patterns of changes at critical points that are shown in the third column. The general patterns of changes at critical points are usually similar for each physical property. This becomes the case even with different types of assembly processes with different building units. But it is not uncommon that a certain pattern of change greatly varies upon even slight changes in assembly conditions. The last column shows whether measuring each physical property is useful for characterizing only primary assembly processes or whether it would be useful to characterize higher-order (hierarchical) assembly processes as well.

There is a review by Patist (2002) that shows various experimental techniques for the determination of the critical micellar concentration (*cmc*) of surfactant solutions. Another review (Söderman et al., 2004) particularly illustrates various nuclear magnetic resonance (NMR) techniques for the characterization of molecular assembly systems. Along with surfactant molecules, amphiphilic block copolymers

TABLE 16-2. Collection of critical assembly parameters that are obtained from the measurements of the physical properties shown in Table 16.1. m, c, b, and b-m refer to molecular, colloidal, biological, and bio-mimetic assembly processes, respectively. p indicates that the parameter can be defined only for primary assembly processes. h indicates that it can be defined for both primary and higher-order (hierarchical) assembly processes.

Parameter	Assembly Process	Assembly Order
critical micellar concentration (*cmc*)	m, b, b-m	h
aggregation number	m, c, b, b-m	h
critical aggregation number (*can*)	c	h
surface critical micellar concentration	m, c, b, b-m	h
counterion binding, dissociation, and dynamics	m, b, b-m	h
monomer exchange dynamics	m, c, b, b-m	h
Krafft point	m	p
HLB (hydrophile–lipophile balance) value	m	p
phase inversion temperature	m	p
critical interaction distance (e.g., critical capillary length)	c	p
kinetics and thermodynamics values	m, c, b, b-m	h

makeup another group of self-assembly systems with important scientific and technological implications. Two articles (Riess, 2003; Zhu and Jiang, 2007) review the detailed characterization techniques for their assembly processes.

16.4. COLLECTION OF CRITICAL ASSEMBLY PARAMETERS

When the measurements of the physical properties shown in Table 16-1 are made for the characterization of assembly processes, the result is typically quantified with a small group of common parameters. When characterizing assembly processes within the homologue series of building units or with a single building unit with systematic control of assembly conditions, these parameters can be directly compared. This usually provides first-hand information on assembly capability and on hierarchical assembly processes (for more examples, see Figures 3-3, 3-4, 3-7, 3-9, 4-3, and 4-4). Also, the parameters can be used to calculate the thermodynamic, kinetic, and dynamic values for the assembly processes and for various simulations. This will be called "critical assembly parameter" here. Table 16-2 collects the critical assembly parameters that frequently appear in the literature. The types of assembly processes where each parameter can be defined are shown in the second column. The third column shows whether each parameter is useful for only primary assembly processes or whether it would be useful for higher-order assembly processes as well. As with those in Table 16-1, these indicate the general aspect of each physical property, and not an absolute condition.

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Part IV

Characterization

15

Assembly Forces and Measurements

15.1. INTERMOLECULAR AND COLLOIDAL FORCES

Intermolecular, intramolecular, colloidal, and surface forces (hereafter referred to as intermolecular and colloidal forces) play vital roles from the self-assembly of simple amphiphiles into micelles to the fabrication of working nanodevices. Compared with covalent bonds, they are relatively weak and their working distances are relatively long. Their origins are diverse, but their strengths and working distances are comparable to each other and often overlap (Israelachvili, 1992; Ninham and Lo Nostro, 2010).

Many of the intermolecular and colloidal forces and their interaction energies can now be obtained with thermodynamic and kinetic methods, and molecular simulations. However, to gain more quantitative understanding of the self-assembly processes and the assembled systems, it is important to have them directly measured. Many different types of measurement techniques have been developed over the past few decades. And their measuring capabilities now reach even more complex situations. For example, the capillary torque of water exerted on silicon plate has been recently measured as 0.1–10 nN·m (Takei et al., 2010). Table 15-2 is a collection of these measurement techniques. Undeniably, the two most widely used are atomic force microscopy (AFM) and surface forces apparatus (SFA). They have been constantly improved with many derived versions and combined with other measurement techniques, and they have produced vast amounts of reliable measurement data across diverse types of intermolecular and colloidal forces

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from many different systems. One of the most important features of these techniques is that they have made it possible to quantitatively measure the strengths of intermolecular and colloidal forces as a function of their working distances. More details are shown in the second section.

There is a special issue of *Langmuir* that highlights the recent progress on the measurements of intermolecular and colloidal forces, and their relevance for many types of applications (Schwartz and Whitten, 2008).

15.2. COLLECTION OF INTERMOLECULAR AND COLLOIDAL FORCES

Table 15-1 collects the intermolecular and colloidal forces that govern self-assembly. As discussed in Chapter 8, most of the forces that are induced by external stimuli have significant impact on assembly processes and assembled systems. Their strengths and working distances are usually comparable to those of intermolecular and colloidal forces. These induced forces are included in the table as well. Each type of force, that is, attractive, repulsive, directional, or oscillatory, is also listed. But note that this listing covers the usual situations, and is not absolute. Depending on conditions, they can vary. Hydrophobic force is the most common and the most important attractive force for self-assembly. Direct measurements of hydrophobic force between hydrophobic surfaces have been conducted for decades. But its true origin is still under debate (Meyer et al., 2006).

15.3. MEASUREMENTS OF INTERMOLECULAR AND COLLOIDAL FORCES

Both atomic force microscopy and surface forces apparatus are useful for direct force measurements of diverse systems including soft and hard surfaces. The greatest advantage of these two techniques over others is that they measure the force–distance curves directly. This can explicitly reveal how the intermolecular and colloidal forces work spatially between the molecules and surfaces, in other words, between the assembly building units. The distance resolution is about the same for both techniques, which is $\sim$0.1 nm. Force sensitivity for both is in the range pN–nN, depending on the nature of the force measuring, but generally atomic force microscopy is more sensitive. Both measure diverse forces, but atomic force microscopy usually has geometrical advantages when measuring intermolecular and intramolecular forces. Surface forces apparatus, on the other hand, has particular advantages when measuring surface and colloidal forces.

15.3.1. Atomic Force Microscopy

Figure 15-1 shows how intermolecular and colloidal forces are measured using atomic force microscopy (AFM)–based techniques. Figure 15-1(a) has the basic

TABLE 15-1. Collection of intermolecular, intramolecular, colloidal, and surface forces that govern self-assembly.

Force	Type
hydrophobic force	attractive
van der Waals force	attractive
electric double-layer force	repulsive
electrostatic force	attractive/repulsive
hydration force	repulsive
solvation force	oscillatory
hydrogen bond	attractive/directional
halogen bond[a]	attractive/directional
critical Casimir force	attractive
coordination (complexation) bond	attractive/directional
host–guest complexation (inclusion)	attractive/directional
size exclusion	attractive/directional
charge transfer	attractive
$\pi-\pi$ stacking	attractive/directional
steric hindrance	repulsive
capillary force	attractive/directional
adhesion force	attractive/directional
depletion force	attractive
centrifugal force[b]	attractive/directional
flow (shear, elongational, vortical)[b]	attractive/directional
gravitational force[b]	attractive/directional
buoyancy force[b]	repulsive/directional
electric force[b]	attractive/repulsive/directional
magnetic force[b]	attractive/repulsive/directional
ultrasound force[b]	attractive/repulsive
hydrodynamic force[b]	attractive/repulsive/directional
electrophoretic force[b]	attractive/repulsive/directional
magnetophoretic force[b]	attractive/repulsive/directional
thermophoretic force[b]	attractive/repulsive
diffusiophoretic force[b]	attractive/repulsive
osmophoretic force[b]	attractive/repulsive/directional
electroosmophoretic force[b]	attractive/repulsive/directional

[a]This is also a directional bond like a hydrogen bond and is slightly stronger than a hydrogen bond.
[b]Forces that are induced by external stimuli.

schematics. This is the case when the AFM tip is attached with a single colloidal particle. But many other tip-derivations are possible depending on the forces that are measured. A full description of force measurements using atomic force microscopy is beyond the scope of this chapter. For experimental details and their comparisons with other techniques, refer to Claesson et al. (1996). There is an excellent study (Lin et al., 2005) that presents direct force measurements focusing on protein–ligand and protein–protein interactions. It also shows a detailed theoretical background of force–distance curves and plenty of actual data. Figure 15-1(b) shows a typical force–distance curve that is obtained by using atomic force microscopy. Forces that are typically measured by atomic force microscopy are van der Waals force, adhesion, capillary force, elastic strength, electrostatic force, and stretching of proteins or polymers. One disadvantage of using atomic force microscopy is that the forces are generated in only one

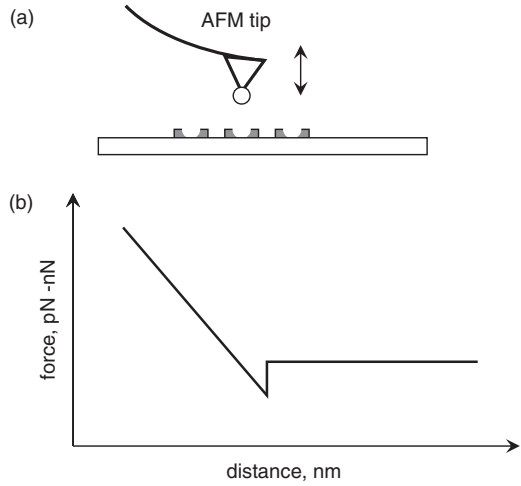

Figure 15-1. Force measurements using atomic force microscopy (AFM)–based techniques: (a) schematic illustration and (b) typical force–distance curve.

direction; there is a vertical force but no lateral force. Single-molecule force spectroscopy (SMFS) is one of the popular derived techniques based on atomic force microscopy. For a direct force measurement in a single molecular level using this technique, refer to Zhang et al. (2008).

15.3.2. Surface Forces Apparatus

Figure 15-2 shows how intermolecular and colloidal forces are measured using surface forces apparatus (SFA)–based techniques. Figure 15-2(a) has the basic schematics. One surface is usually attached on piezoelectric crystal while the other surface is mounted with a force-measuring spring. As with atomic force microscopy, its full description is beyond the scope of this chapter. There is an article by Meyer et al. (2006) that reviews important progress in the measurement of hydrophobic forces using surface forces apparatus. Another review article (Claesson et al., 1996) examines experimental details of direct force measurements using this technique. Figure 15-2(b) depicts a typical force–distance curve. Three examples are shown. A thin solid line is where there is only a repulsive force. A bold solid line is where forces are going through both repulsion and attraction. A dotted line is where forces show oscillatory behavior. Notice that the force in the y-axis is expressed as force/radius (mN/m). There is a study (Frink and van Swol, 2000) that presents some additional theoretical basis for the analysis of force–distance curves. With surface forces apparatus, forces are typically measured between the surfaces in solution. It measures van der Waals force, electric double-layer force, oscillatory force such as solvation, hydration force, hydrophobic force, steric interaction, capillary force, and adhesion (Israelachvili, 1992). One thing to remember when using surface forces apparatus is that both the forces that are imposed and the separations between the two surfaces are variables.

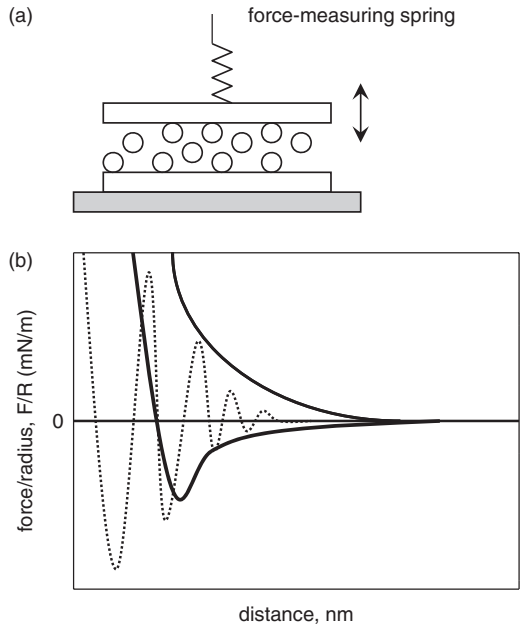

Figure 15-2. Force measurements using surface forces apparatus (SFA)–based techniques: (a) schematic illustration and (b) typical force–distance curves.

15.4. COLLECTION OF MEASUREMENT TECHNIQUES

Table 15-2 collects the experimental techniques that are widely used in the characterization of assembly processes and assembled systems. It has three additional columns. Force measurement indicates their capabilities to measure intermolecular and colloidal forces either directly or indirectly. Remember that only two known techniques (atomic force microscopy and surface forces apparatus) produce measured force–distance curves. The column for assembly process indicates whether each technique can measure and track the critical behaviors of each assembly system. And the third column shows whether each technique can measure the structural properties of each assembled system. Details on the characterization of assembly processes and assembled systems are shown in the next two chapters. These are not absolute conditions. They indicate the acceptable usage of each technique for producing reliable results that are comparable to the theoretical values.

15.5. IMPLICATIONS OF BUILDING UNIT STRUCTURES FOR CHARACTERIZATION

Structural information of assembly building units can assist in selection of the characterization techniques for their assembly processes and assembled systems. The same information can also help us understand and process the experimental data in a systematic manner. Figure 15-3 is designed to show the implications of

TABLE 15-2. Collection of experimental techniques that are widely used for the characterization of assembly processes and assembled systems. o indicates that the technique is useful for measurements of noncovalent forces,[a] critical phenomena during assembly processes, or the structural properties of assembled systems. × indicates that it is not useful for a particular measurement.

Technique	Force Measurement	Assembly Process (Critical Phenomena)	Assembled System (Structural Properties)
surface tensiometry	o	o	x
interfacial tensiometry	o	o	x
conductometry	x	o	x
turbidometry	x	o	x
viscometry	x	o	o
fluorescence spectrometry	x	o	x
UV/Vis spectroscopy	x	o	x
IR spectroscopy	x	o	x
nuclear magnetic resonance spectroscopy (NMR)	x	o	x
photoelectron spectroscopy	x	o	x
scanning electron microscopy (SEM)	x	x	o
transmission electron microscopy (TEM)	x	x	o
small-angle neutron scattering (SANS)	x	x	o
small-angle X-ray scattering (SAXS)	x	x	o
laser light scattering	x	x	o
X-ray diffraction (XRD)	x	x	o
low-energy electron diffraction (LEED)	x	x	o
near-edge X-ray absorption fine structure (NEXAFS)	x	x	o
atomic force microscopy (AFM)	o	x	o
scanning probe microscopy (SPM)	o	x	o
Brewster angle microscopy (BAM)	x	x	o
ellipsometry	x	x	o
surface forces apparatus (SFA)	o	x	x
circular dichrometry	x	o	x
birefringent measurement	x	o	x
UV/Vis irradiation	x	o	x
catalytic reaction	x	o	x
cyclic voltammetry	x	o	x
pH titration	x	o	x
electrophoresis	o	o	x
electroosmosis	o	o	x
magnetophoresis	o	o	x
single-reflection thin-layer ATR spectroscopy	x	o	o
thermal desorption spectroscopy	x	o	x
sorption isotherm (BET, BJH)	x	o	o
surface pressure–area (π-A) isotherm	o	o	x
quartz crystal microbalance	x	o	x

[a]Intermolecular, intramolecular, colloidal, and surface forces from Table 15-1.

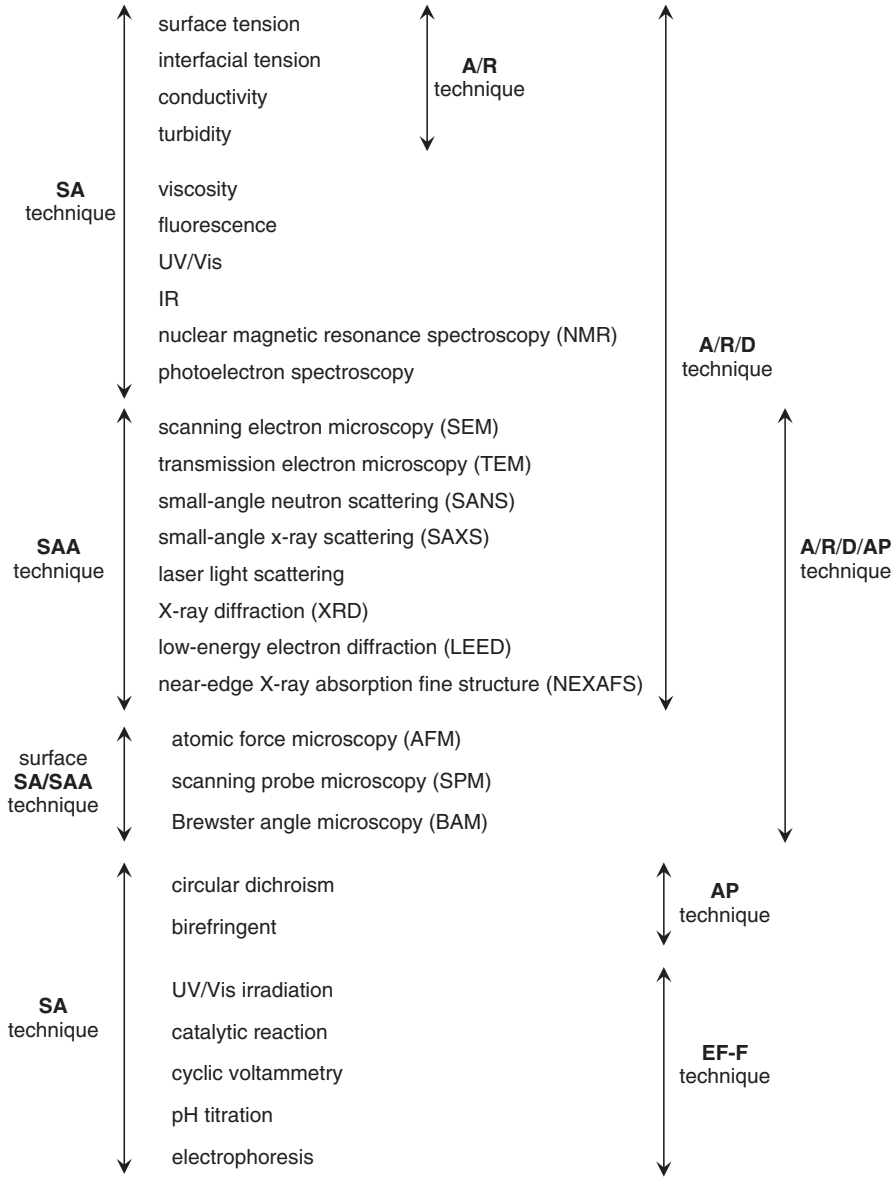

Figure 15-3. Implication of building unit structures for the characterization of assembly processes and assembled systems. **SA** and **SAA** are short for self-assembly and self-assembled aggregate, respectively. **A, R, D, AP**, and **EF-F** refer to attractive, repulsive, directional, asymmetric packing, and external force–specific functional segments, respectively.

building unit structures for these aspects. It classifies some common experimental techniques based on the segmental structures of the assembly building units (for more about *segmental analysis*, see Subsection 1.2.2).

Process techniques (**SA** techniques) are mainly for the detection/confirmation of assembly processes. They can show critical changes in physical properties before and after assembly occurs. Hence, these techniques can be useful whenever there are requirements to determine basic assembly parameters such as *cmc* (critical micellar concentration) and *can* (critical aggregation number). **SA** techniques are widely available, ranging from conventional surface tension measurement to some spectroscopic ones. They can also cover the techniques that allow multiple measurements of different physical properties simultaneously, including irradiation, titration, and some analytical techniques such as electrophoresis.

Structural techniques (**SAA** techniques) usually show no significant differences in physical properties before and after assembly occurs. But they can provide clear structural evidence for the occurrence of the assembly. This evidence can be further used to analyze the dynamic and structural properties of the aggregates. Surface **SA/SAA** techniques are mainly for assemblies on surfaces and surface aggregates. Many microscopy-based techniques belong to these techniques.

A/R techniques are those that can be readily used for the assembly processes of building units that have only attractive and repulsive segments. This is the most fundamental form of assembly. **A/R/D** techniques are for assembly processes of building units that have all three fundamental segments. And **A/R/D/AP** techniques are for assembly systems that have an asymmetric packing segment in addition to the fundamental segments. Some **A/R/D** techniques can cover **A/R** techniques and **A/R/D/AP** techniques. **AP** and **EF-F** techniques are those that can detect/confirm the existence of the asymmetric packing segment and the effect of the external force–specific functional segment, respectively, regardless of the full structures of the building units under study.

Figure 15-3 is designed for assembly processes and assembled systems. It helps pin down the group of techniques that have to be primarily considered and provides preliminary information as to what can be expected from each choice of technique. Their detailed implications for the characterization of each assembly issue are shown in the next two chapters.

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17

Assembled Systems and Structural Properties

17.1. STRUCTURAL PROPERTIES FOR THE CHARACTERIZATION OF ASSEMBLED SYSTEMS

The term *structural property* is so general that it can include a diverse range of properties from pure structural parameters to materials properties. It can also be defined for a general characterization of delicate materials such as biological and bio-mimetic materials. However, in its usual sense, it can be said that the structural properties are those that are commonly used for the characterization of various materials whose exchange dynamics are relatively slow so that their structural integrities and shapes are maintained within the time scale of their characterization. All of the solid materials belong to this. Solid-like materials, such as liquid crystals and many biological objects, are routinely characterized using the term *structural property*.

Assembled systems include self-assembled aggregates, nanoassembled systems, and nanofabricated systems (for details, refer to Section 2.6). Many assembled systems have a dynamic nature but are surprisingly resilient (for additional explanation, see Section 6.2); thus, they well maintain their structural integrities and shapes. This dynamic nature of assembled systems is mainly related to the exchange of individual building units within the assembled systems; this does not alter the structural nature of most assembled systems. Even though the individual building units inside the assembled systems might be constantly exchanged, the structures and detailed structural properties of the assembled systems stay constant. Some assembled

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systems are kinetically arrested systems with less significant exchange dynamics of their building units. Mesoporous materials are a good example (shown in Table 7-2); so are many of the nanofabricated systems (shown in Table 13-4). The morphological sizes of the assembled systems are similar to those of the solid materials that are routinely characterized with common structural properties (for more about structural properties, refer to Table 17-1). Therefore, the common structural properties of solid and solid-like materials can be directly used not only to identify the existence of assembled systems but as a facile guide to fully characterizing the detailed structural features of assembled systems.

The two most widely used techniques for the structural characterization of assembled systems are scattering based and spectroscopy based. These can be used to analyze general structural properties such as morphology, structural transition, size, and size distribution. They can also resolve issues related to local

TABLE 17-1. Collection of structural properties to measure for the structural characterization of assembled systems. p indicates that the property is mainly useful for primary assembled systems. h indicates that it can be useful for both primary and higher-order (hierarchical) assembled systems.

Assembled System	Property	Assembled Order
pore-based systems	pore shape	p
	pore connectivity	p
	pore size	h
	pore size distribution	h
	pore volume	p
	inner surface area	p
	pore alignment	p
particle-based systems	particle shape	p
	particle size	h
	particle size distribution	h
	structural phase transition (polymorphism)	p
	particle symmetry	p
film-based systems	surface structure	h
	interfacial structure	h
	surface roughness	p
	surface coverage	p
	surface thickness	p
	hydrophobicity	p
	hydrophilicity	p
	superhydrophobicity	p
	superhydrophilicity	p
	wettability	p
	surface reactivity	p
coupled systems	surface area	p
	hierarchy	h
	chirality	h
	helicity	h
	fractal dimension	h
	packing geometry	p
	flexibility	p
	stiffness	p
	hardness	p
	tensile strength	p

viscosity, local ordering, degree of packing, and degree of hydration, depending on the system. There are two comprehensive reviews (Mortensen, 2001; Vasilescu et al., 2001) that examine the general aspects of these two techniques for the characterization of assembled systems. These articles show the related theories for each method, sample preparations, data analyses, and instrument step-ups as well. The main systems they reviewed are the assembled systems of block copolymers and nonionic surfactants. But the detailed issues can be directly generalized to other assembled systems. The second article (Vasilescu et al., 2001) further shows how molecular probe methods for some spectroscopy-based techniques can provide reliable structural properties of assembled systems.

17.2. CHARACTERIZATION PRINCIPLES

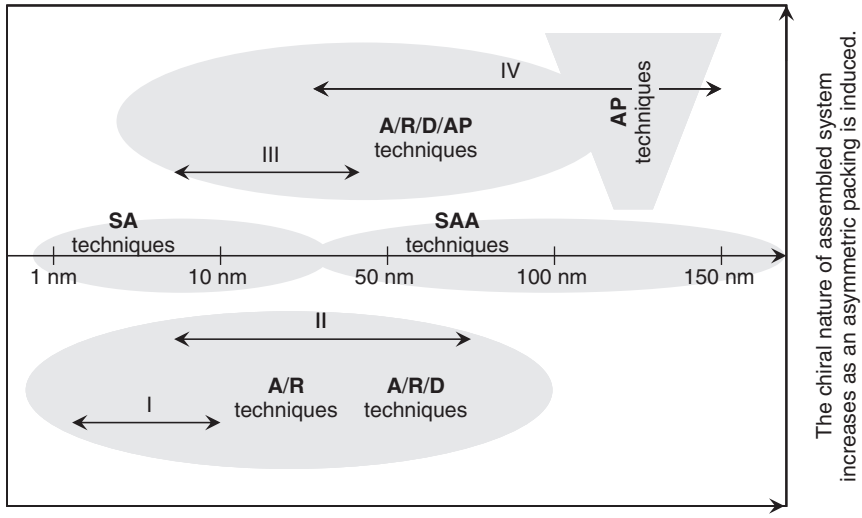
Section 16.2 showed that the characterization of assembly processes can be effectively guided using the structural information of assembly building units. This section shows that the structural characterization of assembled systems can be guided the same way. As with the discussion in Section 16.2, it does not cover the full scope of experimental techniques available, but shows how the concept of segmental analysis can contribute to actual experiments (for more about *segmental analysis*, see Subsection 1.2.2).

17.2.1. Structures of Primary Assembled Systems

Figure 17-1 shows the experimental guide for characterizing the primary structures of assembled systems. This general guide is valid for assembled systems formed both in solution and at surface. The format is somewhat different from that of Figures 16-1 and 16-2. The horizontal axis is now for the size of the primary assembled system. As it goes to the right-hand side, it is assumed that the size increases as a result of more directional force. The vertical axis expresses the chiral nature of the primary assembled system. It is assumed that the chiral nature is expressed more as the degree of asymmetric packing increases. The numbering with capital letters parallels that in Figures 5-1, 5-3, 5-4, and 5-6.

17.2.1.1. Molecular Systems. Figure 17-1(a) depicts the assembled systems of molecular, bio-mimetic, and biological building units. The size of the horizontal axis ranges from ~1 nm to ~150 nm, which covers most of the building units of these types. When the sizes of the building units are in the range of a few nanometers to a few tens of nanometers, the process techniques (**SA** techniques) from Figure 15-3 might be the most suitable ones for the characterization of their primary assembled systems. However, when their sizes are increased beyond a few tens of nanometers, the structural techniques (**SAA** techniques; also from Figure 15-3) become more practical. Even though it is the assembled systems of molecular building units to be characterized, when their sizes become comparable with the colloidal length scale, it begins to impose a number of practical limitations

(a) Molecular, bio-mimetic, and biological assembly building units



(b) Colloidal assembly building units

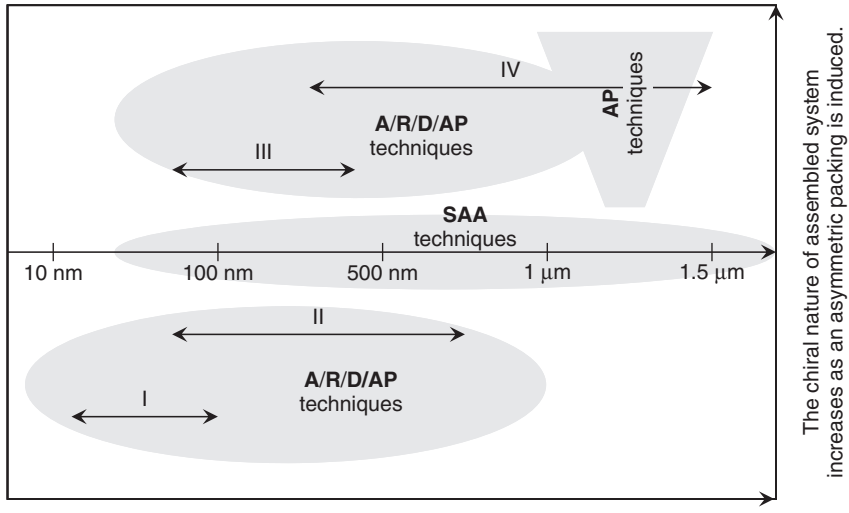


Figure 17-1. Experimental guide for the characterization of the primary structures of assembled systems. (For the abbreviations of each technique group, see Figure 15-3.)

on the **SA** techniques. It is the same logic as in Figures 16.1(b) and 16.2(b) that colloidal particles do not induce enough physical properties that can be traced with the **SA** techniques. A direct observation with the **SAA** techniques simply becomes more practical in most cases.

For assembled systems that belong to example I of Figures 5-1, 5-3, and 5-4, a simple measurement with the **A/R** techniques (from Figure 15-3) followed by proper data analysis can provide a clear structural picture of them. When the directional segment is involved (those belonging to example II), the **A/R/D** techniques become more practical. The **A/R** techniques can provide some idea about the directionality of the assembled systems. But it is usually somewhat limited, even though this is one of the reasons that the **A/R** techniques are viewed as a part of the **A/R/D** techniques in Figure 15-3. More directional force usually means bigger assembled systems. A selection of direct observation techniques from the **A/R/D** techniques may more practical when this is expected for a given system.

For assembled systems that belong to example III, detection of the morphological characteristics induced by the asymmetric packing segment is critical. The **A/R/D/AP** techniques are suitable for this purpose. They can provide some additional structural parameters as well. When asymmetric packing is the central issue, the **AP** techniques can be used. These do not provide the detailed structural features that the **A/R/D/AP** techniques do; however, they often become the essential tool for full characterization of asymmetrically packed systems, especially when a quantitative analysis of the degree of the asymmetric packing is required.

For those that belong to example IV, there is not much difference from those belonging to example III. Proper combination of **A/R/D/AP** techniques with **AP** techniques is important. Since this last example is usually much bigger than the others, direct imaging techniques are often more useful. The **A/R/D/AP** techniques surely cover many **A/R/D** techniques. But not all of the **A/R/D** techniques can cover the **A/R/D/AP** techniques, especially when an asymmetric packing segment is strongly expressed.

17.2.1.2. Colloidal Systems. The characterization guide for the colloidal assembled systems shown in Figure 17-1(b) is basically the same as for the molecular systems. The length scale of the horizontal axis, however, is now from $\sim$10 nm to $\sim$1.5 μm. This is an arbitrary setting but enough to cover the sizes of most of the primary colloidal assembled systems.

Most **SA** techniques do not work properly for colloidal assembled systems. Neither do the **A/R** techniques. And not all of the **A/R/D** techniques work for them, either. Most of the colloidal building units are simply too big, and many of them do not generate enough physical properties that can be measured mainly because of this size issue. Their assembled systems are even bigger. For assembled systems that belong to examples I and II of Figures 5-1, 5-3, and 5-6, the most suitable way to characterize their structures is using the **A/R/D/AP** techniques even though their building units do not have an asymmetric packing segment. The same goes for those belonging to examples III and IV. But the role of the techniques that can detect the morphological characteristics induced by the asymmetric packing segment becomes

important. Proper combination with the **AP** techniques is important, too. The **SAA** techniques are handy for most colloidal assembled systems because of their sizes. Direct imaging with precise details and the subsequent extraction of structural parameters become easier as they get bigger.

17.2.2. Structures of Higher-Order Assembled Systems

Figure 17-2 shows the experimental guide for characterizing the higher-order structures of assembled systems. This general guide is valid for assembled systems formed both in solution and at surface. The numbering with capital letters parallels that in Figures 5-2, 5-7, 5-8, and 5-9.

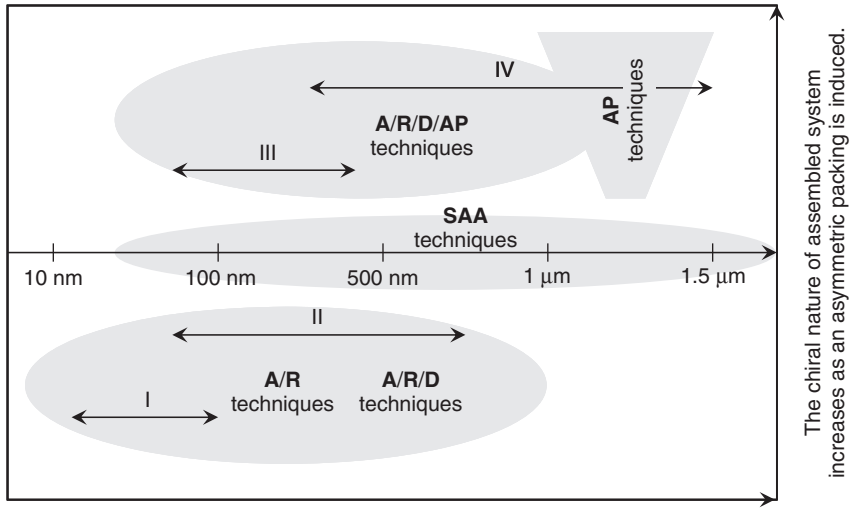
Figure 17-2(a) depicts the assembled systems of molecular, bio-mimetic, and biological building units. Figure 17-2(b) illustrates those of colloidal building units. The format is almost the same as that of Figure 17-1. A key difference is the length scale of the horizontal axis, which is now ten times larger. This is to cover bigger and more diverse natures of higher-order assembled systems. But for this very reason, the **SA** techniques are not useful for higher-order assembled systems. Imaging techniques are a lot more useful than the process techniques. The general characterization guide for the higher-order assembled systems is almost the same as for the primary systems. Thus, most of the techniques chosen in Figure 17-2 are the same as those in Figure 17-1. When asymmetric packing is expressed, it is usually necessary to analyze the data from the **A/R/D/AP** techniques combined with the **AP** techniques.

There is an article (Mortensen, 2001) that reviews the formation of the hierarchical structures of assembled systems, and their hierarchy, structural transitions, and characterization. An article by Iengo et al. (2003) reviews the characterization of assembled systems of porphyrins by using NMR spectroscopy and X-ray crystallography. It includes the structural transitions of the assembled systems and the higher-order (hierarchical) assemblies and structures as well. What is unique in this article is that the assembled systems are formed by metal-driven (or coordination bond–directed) assemblies, which are often called *supramolecular* assemblies.

17.2.3. Hierarchy and Chirality

Figure 17-3 shows the characterization guide for the hierarchy and chirality of assembled systems. As with the previous two figures, this general guide is valid for assembled systems formed both in solution and at surface. It also works for most building units, including molecular, bio-mimetic, biological, and colloidal ones. The numbering with capital letters parallels that in Figures 6-1, 6-2, 6-3, 6-4, and 6-5. On the horizontal axis, multi-step assembly is induced as it goes to the right-hand side. The most typical factor for inducing multi-step assembly is the increasing concentration of building units, which was assumed for all four examples here. However, there are many other factors that can induce multi-step assembly, including changes in pressure or temperature, changes in solution conditions such as pH and ionic strength, addition of counterions, and changes in geometrical factors

(a) Molecular, bio-mimetic, and biological assembly building units



(b) Colloidal assembly building units

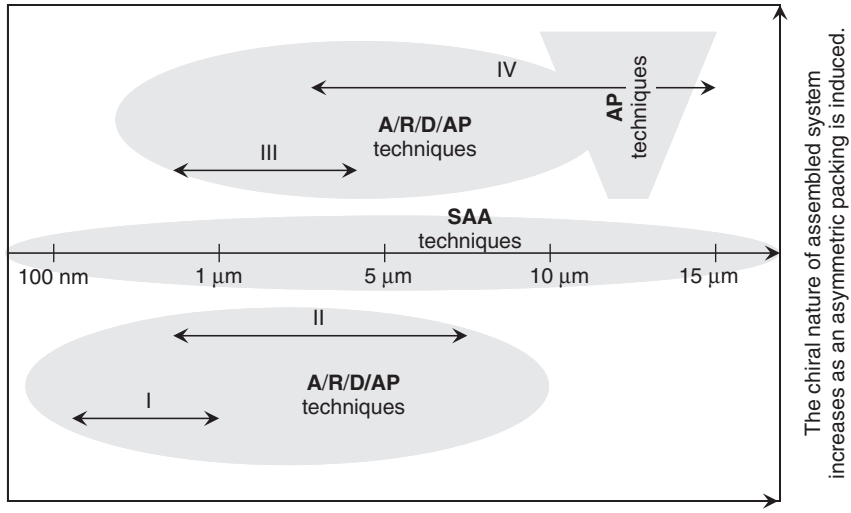


Figure 17-2. Experimental guide for the characterization of the higher-order (hierarchical) structures of assembled systems. (For the abbreviations of each technique group, see Figure 15-3.)

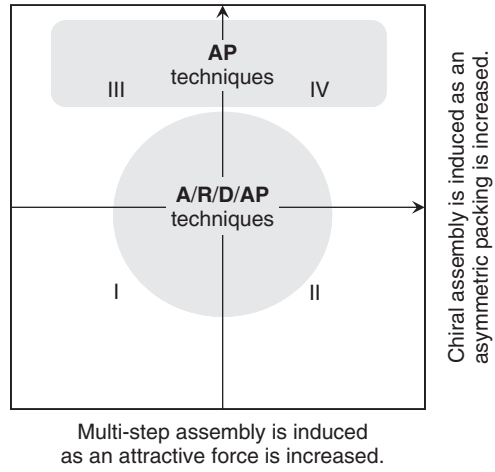


Figure 17-3. Experimental guide for the characterization of the hierarchy and chirality of assembled systems. (For the abbreviations of each technique group, see Figure 15.3.)

such as confinement. Whichever factor is used to induce multi-step assembly, once it is suggested that it can take place, this general direction on the horizontal axis can be followed to characterize it. On the vertical axis, chiral assembly is induced as it goes upward. For most cases, it is the asymmetric packing segment that induces the chiral assembly. However, other conditional factors such as interaction with surfaces or local concentration fluctuation can induce chiral assembly as well, even with primary building units that do not have any asymmetric packing segment. As with the horizontal axis, whichever factor induces the chiral assembly, this general direction can be followed to characterize it.

For all four examples, the **A/R/D/AP** techniques should work to determine both hierarchy and chirality not only for the primary assembled systems but for the higher-order systems as well. Since the focus here should be on the morphological characteristics after the assembly is confirmed to have taken place, most of the **SA** techniques, which include the **A/R** techniques, usually do not work. It might be possible to deduce some structural information with the help of modeling but in a limited way. Whenever chirality is strongly expressed, proper combination with the **AP** techniques is necessary. This helps to obtain more reliable experimental confirmation.

There is an article (Lee, et al., 2009) that reviews the experimental details for the characterization of chirality, helicity, and other structural properties of assembled systems using circular dichroism (CD) spectroscopy and other techniques. This article also discusses some aspects of the implication of building unit structures for the characterization of assembled systems (for more details, refer to Section 15.5). In addition, it shows the importance of multiple characterization using complementary techniques in order to ascertain a full structural analysis. There is a special issue of *Chemical Society Reviews* (Amabilino, 2009) that has a wider range of

review articles that discuss chiral assemblies and chiral assembled systems, and the characterization of them.

17.2.4. Effect of External Forces

Figure 17-4 shows the characterization guide for the effect of external forces on assembly processes and the structures of assembled systems (for the principles of external force–induced assemblies, refer to Section 9.3). It consists of three steps that are encompassed in one technique group. Once the building unit is selected, the first step is always to identify its assembly processes. Key assembly parameters should be extracted in this first step. It includes critical micellar concentration (*cmc*), aggregation number, the physical properties of counterions (for molecular, bio-mimetic, and biological building units), and critical aggregation number (*can*: for colloidal building units). Whenever necessary, multi-step assembly processes have to be characterized as well. The detailed experimental guidelines for this first step are given in Figures 16-1 and 16-2. The second step is the determination of the structural characteristics of each assembled system. Once the assembly processes and their assembly orders are identified, there should be assembled systems of each order. Figures 17-1 and 17-2 showed the details for the characterization of the primary and higher-order structures, respectively. The third step is the characterization of the hierarchy and chirality of each assembled system. Figure 17-3 provides the details.

What is important for the characterization of the effect of external forces is that they can impact any of the steps of the characterization process. This means that the external force–specific functional techniques (**EF-F** techniques) from Figure 15-3 have to be simultaneously at work in every step of the characterization. Some **EF-F** techniques can perform some tasks that can be done with **SA** techniques. But, in most cases, the **EF-F** techniques do not have the capability to perform any of the characterization at any step. And the **EF-F** techniques

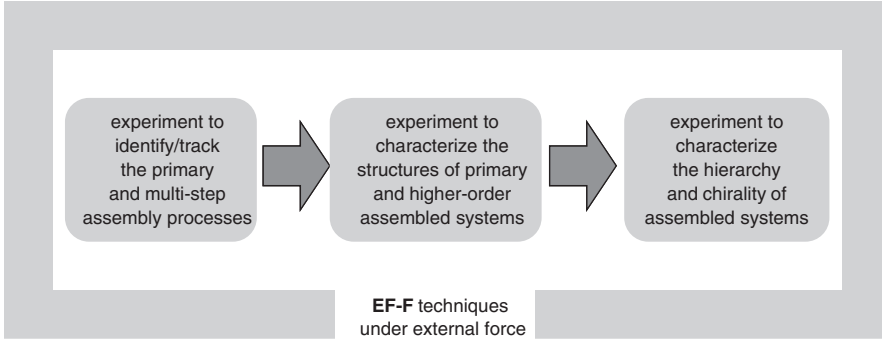

experiment to identify/track the primary and multi-step assembly processes
experiment to characterize the structures of primary and higher-order assembled systems
experiment to characterize the hierarchy and chirality of assembled systems
EF-F techniques under external force

Figure 17-4. Experimental guide for the characterization of the effect of external forces on assembly processes and the structures of assembled systems. (For the abbreviation of the technique group, see Figure 15-3.)

are usually preselected. The external force to be used is usually our choice. For external force–induced assemblies, especially with some technological issues, the option to use multiple numbers of functional segments should be more actively explored. Whatever the actual case might be, the technical comparability between the **EF-F** techniques and other techniques should be carefully examined. For example, most of the **EF-F** techniques shown in Figure 15-3 can be set up with most of the **A/R** techniques on a single bench. However, there might be technical difficulties with many of the **SAA** techniques.

17.2.5. Functional Assembled Systems

Figure 17-5 shows the characterization guide for functional assembled systems (for the assembly principles of functional assembled systems, refer to Section 10.3). It also consists of three steps. This is the same as the one in Figure 17-4, which showed the effect of external forces. The important difference, however, is the method of applying the functional techniques (**EF-F** techniques). For the functional systems here, the **EF-F** techniques do not need to be present at all times. They can be brought into any of the steps whenever necessary.

Whenever a new assembly system is designed, the first step is to determine whether it actually self-assembles under a given condition—the primary processes first, followed by multi-step processes. The next step is to characterize the structures of the primary and higher-order assembled systems. Key structural parameters should be obtained here. This includes the symmetry of the assembled systems, morphological defects, structural integrity, and structural flexibility. In addition, some functional parameters can be obtained as well. This includes the permeability of the assembled systems if they have planar shape, the degree of the structural fluctuation, microviscosity, and the degree of interaction with foreign substances such as micellar solubilization. The final step characterizes the hierarchy and chirality of the assembled systems. Many important functionalities related to these structural

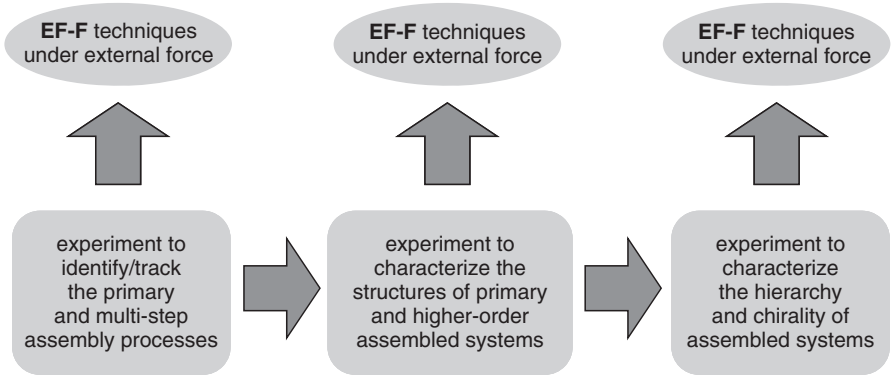

EF-F techniques under external force
EF-F techniques under external force
EF-F techniques under external force
experiment to identify/track the primary and multi-step assembly processes
experiment to characterize the structures of primary and higher-order assembled systems
experiment to characterize the hierarchy and chirality of assembled systems

Figure 17-5. Experimental guide for the characterization of functional assembled systems. (For the abbreviation of the technique group, see Figure 15-3.)

features should be carefully examined at this step. A great deal of optical, spectroscopic, and crystallographic properties can be controlled with these structural features.

17.3. COLLECTION OF STRUCTURAL PROPERTIES TO MEASURE

Table 17-1 lists various structural properties that can be measured for the structural characterization of assembled systems. These are the ones that appear frequently in the literature. This table works for most molecular, colloidal, biological, and bio-mimetic building units. But note that there is always a possibility that a certain property works better than the others depending on the types of building units and assembled systems. For example, for certain types of pore-based systems such as mesoporous silicas and mesoporous carbons, all the properties shown in the table can be useful for the characterization of their structural features. But for certain other types of pore-based systems, such as activated carbons, aerogels, and xerogels, their structural features can be analyzed mainly with pore size distribution, pore volume, and inner surface area. The properties of each of the pore-based, particle-based, and film-based systems are almost exclusive to each type of system. Those properties that are for pore-based systems can rarely be used for structural analysis of the other two types of systems.

The same is true for the properties of the other types of systems. Coupled systems indicate assembled systems that are composed of either two or all three types of pore-, particle-, and film-based systems. Thus, properties that are shown for characterization of coupled systems can be applied to all three types of systems. The p in the third column indicates that the property is mainly useful for characterization of primary assembled systems. The h indicates that the property can be useful for characterization of both primary and higher-order (hierarchical) assembled systems. For example, for pore-based systems, different pore sizes and their different distributions can suggest that the assembled system under characterization might have hierarchical structures, but other properties cannot. As another example, for coupled systems, the measurements of hierarchy, chirality, helicity, and fractal dimension can clearly say whether the assembled system under characterization has only primary structure or whether it is composed of higher-order structures as well. The other properties can hardly be used to say that there are higher-order structures within the assembled system. The properties could have originated only from the primary structure of the assembled system or they could be those that are averaged out of all the primary and higher-order structures within the assembled system.

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18

Modeling and Simulations

18.1. ASSEMBLY SYSTEMS ARE BIG AND MULTI-SCALED

Reliable models and simulation techniques that can be used to predict desired end structures and properties of self-assembly and nanotechnology systems are critical. Not only can they be complementary with the experimental characterization described in the previous three chapters, but they can often reveal structures and properties that otherwise cannot be accessed by the experiments. There have been diverse works to model the classical assembly processes and assembled systems. There are thermodynamic, geometric, and elastic models. For surface assembly and nanopore-based systems, a number of isotherms have been developed. In addition, typical scattering models (from light to small-angle X-ray and neutron) and a number of spectroscopic models, including nuclear magnetic resonance (NMR) and many others, have been borrowed and even modified for assembly systems. Most of these models are primarily valid for primary assembly processes and primary assembled systems. This chapter will not discuss all of these, but a brief review will be given in the second section.

There have been tremendous advances over the past two decades in simulation works. In comparison to the typical simulation works for systems of small size, there are two key issues on which to focus when simulating assembly processes and assembled structures. First, the number of atoms or molecules that are involved is very large, which simply means that the simulation systems are big. Second, their processes, structures, and properties almost always have multi-scaled

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time and length origins. For example, the exchange dynamics of individual assembly building units with simple spherical assembled aggregates such as surfactant micelles are faster than the dynamics of the assembled system itself, which usually has many orders of magnitude difference. Multi-step assembly of individual collagen building units into macroscopic collagen fiber takes places through many orders of different length scales. And binary colloidal crystals, which are typical colloidal assembled systems, are often assembled with the size differential of the colloidal building units having two to three orders of magnitude difference. A full degree of simulation taking all these multi-scale issues into account is simply too expensive. This chapter presents the relevance of diverse simulation techniques for understanding assembly processes and assembled systems, mainly focusing on how to incorporate these key issues during the simulations without losing too much information. This chapter does not touch on the details of each simulation technique, which would be impossible to cover with a single chapter. It does not cover simulation works that study the synthetic mechanisms of nanostructures, either, such as the catalytic growth of carbon nanotube, fullerene, or graphene, since these are assemblies of atoms through covalent bonds. The main focus of this chapter is the assembly processes and assembled systems of those nanostructures.

18.2. CLASSIC MODELS

18.2.1. Thermodynamic Models

The two most celebrated thermodynamic models in the field of self-assembly are pseudo-phase separation and mass-action models. These are mainly for self-assembly of molecular building units in solution. The pseudo-phase separation model expresses the monomeric phase and the aggregate (micellar) phase as if they were two different phases and there is a phase separation and transition between the two. The mass-action model, on the other hand, expresses the formation of the aggregates as if it were a reaction of a certain number of monomers. But both models produce the same form of the thermodynamic equation, which elegantly correlates the standard free energy of micelle formation with the critical micellar concentration (*cmc*). Full details can be found in Section 3.3 of Lee (2008). They were originally developed for surfactants but turned out to be useful for many other amphiphiles, such as amphiphilic copolymers.

18.2.2. Colloidal Model

Another much-celebrated classic model is DLVO (Derjaguin-Landau-Verwey-Overbeek) theory. This is exclusively for assembly of colloidal particles in solution. This model expresses the total force acting on each colloidal building unit as the sum of electric double-layer and van der Waals forces. It clearly describes the critical aggregation number (*can*) for colloidal assembly, as well as colloidal stability and coagulation. More details are in Section of 2.2 of Lee (2008).

18.2.3. Geometrical Model

This model is commonly known as *surfactant packing geometry*. It was originally developed for self-assembly of surfactant molecules, by purely considering the molecular geometry of the building units and the geometrically optimal packing for their assembly. This model later found its validity for many other building units, including colloidal particles of diverse shapes, as long as their geometry can be estimated. This model is very useful for understanding the formation of assembled systems and their structural transformation, both in bulk solution and at surface. But it has some limitations when predicting the structures of assembled systems. For example, an amphiphilic building unit can form either spherical micelle or hexagonal liquid crystal even with the same value of packing geometry (g-value), depending on the assembly conditions. There must be careful consideration of assembly conditions such as temperature, pressure, concentration, pH, and ionic strength. Section 3.4 of Lee (2008) has more details.

18.2.4. Elastic Model

This model was originally developed for the bilayers as a form of Helfrich Hamiltonian, by taking the elastic properties of the lipid bilayers into account (Helfrich, 1973). The structural parameters of assembled systems are well modeled into this equation, which greatly helps in understanding not only the model membranes and vesicles but biological membranes as well. It is also quite valid when designing artificial membranes with desired functions and properties.

18.2.5. Isotherms

Most of the isotherms were mainly developed for the study of the surface behaviors of atoms and molecules. But over time they have proven useful for the study of assembly processes and assembled systems on surface and interface. Their uses now span many different types of building units including molecular, biological, bio-mimetic, and colloidal. The famous surface pressure–area isotherms provide rich information for assemblies on liquid surface during the formation of Langmuir monolayers. Section 6.3 of Lee (2008) and references therein have more details. For nanopore-based assembled systems, two adsorption isotherms, BET (Brunauer-Emmett-Teller) (Brunauer et al., 1938) and BJH (Barrett-Joyner-Halenda) (Barrett et al., 1951), are widely used almost as standard methods.

18.3. SIMULATIONS

Diverse simulation techniques have been developed for various types of systems. This section will focus on their usefulness for self-assembly and nanotechnology systems. When properly done, simulations can provide many important advantages for the characterization of self-assembly and nanotechnology systems. These include the following:

1. Simulations can reveal both the static and dynamic events of assembly processes (kinetic pathway of assembly, disassembly, and reassembly), by allowing us to take snapshots.
2. They can provide the energetics of assembly processes and assembled systems, by permitting analysis of the parameters that control the assemblies.
3. They can provide a detailed understanding of the relationship between the structures of assembled systems and their properties and functions.
4. This in turn can help in understanding the experimental results and even guide the experiments so that they can assist in designing new assembled systems.

Simulations can now be done not only for single-step assemblies but for more complicated assemblies as well, including hierarchical, chiral, and surface assemblies. But the challenges remain. One of the most critical ones is that there is still a lack of techniques that can predict the macroscopic behaviors of assembled systems and the correlation between parameters and their properties and functions. A more fundamental challenge is of course that self-assembly and nanotechnology systems are inherently multi-scale systems. Vvedensky (2004) presents detailed procedures for the mathematical calculation and algorithmic development of diverse simulation techniques. McCullagh et al. (2008) review the general aspects of simulation of self-assembly processes. For molecular modeling and simulations in general, refer to Hinchliffe (2003) and Rapaport (2004).

18.3.1. Electronic Simulations

Electronic (or quantum) simulations provide the finest resolution among all available simulation techniques by solving many-electron problems. The two main theories for these are the density functional and mean-field theories. And two main calculation methods based on this quantum mechanics are *ab initio* and semi-empirical calculations.

18.3.1.1. Density Functional Theory. Density functional theory (DFT) used to be called Kohn-Sham-Hohenberg theory. This is the most widely used quantum simulation method. It treats the energy of a simulation system with a function of the electron density. It is proven to be very effective for many atomic systems, and offers a quantum mechanical description of electrons and nuclei of the system. Density functional theory has proven useful for the prediction of many nanostructures, including fullerenes, carbon and other nanotubes, and quantum dots, and also for many nanoproperties (Marzari, 2006), including band structure, optical absorption band gap, cohesive energy, catalytic property, and current-voltage characteristics. But this method is limited by the so-called *bottleneck issue* that is common to most of the DFT calculations. Its reliability is limited to systems with a few hundreds of atoms. In addition, even though there have been some recent advances, this method cannot properly address most intermolecular and colloidal forces, which are the key assembly forces. This is especially the case for van der Waals force,

which is the most important and abundant attractive force for most assembly systems. These limitations mean that density functional theory is rarely applied to assembly systems except for small ones.

18.3.1.2. Mean-Field Theory. This is also known as self-consistent field (SCF) theory. It is primarily a statistical mechanical method of addressing combinatorial issues when solving the Hamiltonians of many-body systems. As with density functional theory, this theory is very effective for many atomic systems, and has also proven useful in the study of nanostructures, such as for calculating electronic structures of semiconductor nanoparticles. However, this theory has the same limitation issues of system size as density functional theory, which means it is rarely used for assembly systems. There are some studies that develop coarse-grained simulations based on mean-field theory for specific assembly systems (Ganesan et al., 2010).

18.3.2. Atomistic Simulations

Atomistic simulation basically takes all of the atoms in the simulation system and calculates the structure that has the lowest energy. When done properly, this method can provide rich atomic-level information on processes and structures for many assembly systems. But its uses are still limited to the uniquely atomistic phenomena such as point defect, dislocation, lattice energy, crystal structure, and grain boundaries.

18.3.2.1. Molecular Dynamics and Monte Carlo Methods. Calculations for atomistic simulations are mainly done with either molecular dynamics or Monte Carlo methods. There are also a number of hybrid and derived techniques such as the kinetic Monte Carlo method and the grand canonical Monte Carlo method. The molecular dynamic method allows the atoms and molecules to interact with each other for a period of time. The Monte Carlo method, which is a stochastic method on the other hand, repeats random sampling to calculate the result. Their uses are also limited by the size of the simulation systems. Even though they can handle much larger systems than density functional theory can, it is still not enough for most assembly systems. Typical system sizes for molecular dynamic simulations are limited to fairly small systems with a typical time scale of nanoseconds. Software development has been very active for atomistic simulations. One popular atomic-level force field is CHARMM (Brooks et al., 1983). AMBER, GROMOS, GROMACS, TraPPE, and OPLS-AA are other widely used atomic-level force fields. Guvench and MacKerell (2008) provide a general review of them. The term *force field* refers to the mathematical equations combined with all related molecular parameters.

18.3.3. Coarse-Grained Simulations

Once again, the biggest hurdle for simulations of self-assembly and nanotechnology systems is that they are simply too big as far as simulation methods are concerned.

This means the molecular dynamics method requires a very long simulation time to find the structure, and the Monte Carlo method has to check an enormous number of different structures. Both greatly limit the ability of the atomistic method to come up with a reliable result. There have been many efforts to develop methods that can perform more efficient calculations by overcoming this oversize issue. The coarse-grained (or *mesoscopic*) model is the most widely accepted one. This model takes a couple of atoms within the simulation system and groups them into a "bead" (often called "segment" or "pseudo-atom"). It then uses molecular dynamics or the Monte Carlo method to calculate the structures and properties of the coarse-grained system. It averages the interactions between the beads, not between the atoms, which makes efficient computation possible by simplification. Thus, it allows simulations over sufficiently different length scales for self-assembly and nanotechnology systems and can reveal multi-scale hierarchical structures. The atomic detail is inherently missing from this method, but it can bridge the atomic scale with macroscopic scale. Ultimately, when using coarse-grained models, it is important to adjust simulation parameters through consistent comparison with experimental results and atomic-level simulation values.

Many different types of coarse-grained models have been developed. And each model is designed to address a specific system to resolve a specific issue; thus, each one has its own strengths and its own weaknesses. Schmid (2009) reviews how generic coarse-grained models are used for simulation of amphiphile self-assembly and for formation of mesophases. These models express the amphiphiles as if they were composed of two blocks (segments). Then they assign the beads for each block and perform the calculations as the tail beads (hydrophobic block, attractive segment) attract each other and the head beads (hydrophilic block, repulsive segment) repel each other. Balazs (2007) shows how effective coarse-grained models can be in predicting the equilibrium and dynamic properties of heterogeneous assembly systems (for more about heterogeneous assemblies, see Chapter 7). This article also presents the effect of surfaces and external stimuli (confinement, flow, and light) on their single-step and hierarchical assemblies.

18.3.3.1. Dissipative Particle Dynamics. Dissipative particle dynamics (DPD) expresses the liquid where assembly systems reside as an ensemble of liquid particles so that it can bring the effect of liquid within the simulation scheme. This famous coarse-grained technique was first developed by Hoogerbrugge and Koelman (1992), and is now widely used for the study of mesoscopic properties. It has proven effective for simulation of assembly processes and assembled systems for both molecular and colloidal building units. Hong et al. (2010) successfully used this technique to simulate disassembly and reassembly of block copolymer spherical micelles. Whittle and Dickinson (2001) simulated assembly of spherical colloidal particles by introducing the depletion force into the scheme of force balance. For a comprehensive review of dissipative particle dynamics, see Groot and Warren (1997).

18.3.3.2. Patchy Particle Model. This model expresses (coarse-grains) a colloidal particle or nanoparticle as a couple of beads to improve simulation efficiency.

The liquid is largely ignored. It was mainly developed for self-assembly of colloidal particles and nanoparticles (Zhang and Glotzer, 2004). But it finds usefulness for large molecules such as globular proteins as well. A *patchy* particle is a particle whose surface is decorated with specific interaction sites whose interaction can be either attractive or repulsive. By allowing simulation of colloidal particles or nanoparticles with diverse types of patchy patterns, this method is effective not only for single-step symmetric assembly but for more complicated assemblies including multi-step, directional, hierarchical, and chiral. This method also allows incorporation of selective, directional, and anisotropic interactions between the particles. This feature is very powerful for structural characterization of assembled systems. It can predict the structures of assembled systems formed from the particles with a particular pattern of attractive and repulsive forces. Critical behaviors during the assembly processes can be observed, too. Another important feature of this method is that it can be easily modified for simulation of nonspherical particles such as rods, cubes, and plates, by simulating the particles with anisotropic patches (Zhang and Glotzer, 2004). Doppelbauer et al. (2010) make further advancements in this model by applying the optimization technique based on the genetic algorithm, which makes it possible to identify the ordered structures within assembled systems.

18.3.3.3. Brownian Dynamics. Brownian dynamics is a kinetic model. It expresses the motion of colloidal particles and nanoparticles with the Langevin equation for their assembly (Ermak and McCammon, 1978). The flow of the liquid that surrounds the particles is ignored. This method is effective for simulation of colloidal particles and nanoparticles for both spherical and nonspherical shapes. But, as with the patchy particle model, it can be applied to large molecules such as proteins, peptides, and polymers as well. Wang et al. (2006) report Brownian dynamics simulation of self-assembly of surfactant-coated nanoparticles. Surfactant-coated nanoparticles, by the way, are among the most widely used building units for nanotechnology systems. This work reveals the detailed interplay processes between the attractive and repulsive forces during assembly, which in turn can be a great benefit for further design of nanotechnology systems with various surface-modified nanoparticles.

18.3.3.4. BRAHMS. BRAHMS is another coarse-grained model that is gaining popularity. It is developed by Essex group (Orsi et al., 2008). They present a thorough simulation work for self-assembly of hydrated dimyristoyl phosphatidylcholine into bilayers. This work beautifully shows how a properly developed coarse-grained model can reproduce such a wealth of experimental parameters while using fewer computational resources than atomic-level methodology. They grouped (coarse-grained) the 118 atoms within the lipid molecule into 10 coarse-grain sites. They further refined and extended this model for self-assembly of dioleyl phosphatidylcholine, which has more tricky hydrocarbon structures (one double bond on each hydrocarbon chain), by coarse-graining 138 atoms into 12 coarse-grain sites (Orsi et al., 2010). This work produces properties that are difficult to

obtain experimentally, including pressure distribution, spontaneous curvature, and the diffusion pattern of individual molecules.

18.3.3.5. MARTINI. MARTINI was developed by Marrink group (Marrink et al., 2004; 2007). Four heavy atoms on average are coarse-grained as a single bead in this model. Their simulation works for lipid bilayers and bilayer/cholesterol systems (Marrink et al., 2007) generate a number of thermodynamic and structural properties as well as their structural transformations. They also explain the important steps to follow during coarse-graining and certain limitations when using coarse-grained models. MARTINI is an increasingly popular coarse-grained model for a wide range of amphiphilic and biological molecules.

In addition to those described in this subsection, there are a number of other mesoscopic models that were developed for assembly of colloidal particles. These include moving particle semi-implicit method, fluctuating Navier-Stokes equation, fluid particle dynamics, lattice Boltzmann equation, and stochastic rotation dynamics. Fujita and Yamaguchi (2010) provide a comprehensive review of them.

18.3.4. Continuum Simulations

This technique ignores the atomic structure of the systems completely, instead using mass density, which is assumed to be continuous. This reveals the macroscopic structures and properties of materials over a longer period of time, as well as their phase transitions. The finite element method is the most popular continuum method.

18.3.5. Multi-Scale Simulations

Again, as discussed in the first section, self-assembly is a process that operates over a vast range of length and time scales. And self-assembled systems have their structures over multi-orders of length scales. Thus, the nanotechnology systems that are mostly assembled with self-assembly principles have inherently multi-scale structural natures, and their assembly becomes multi-scale processes as well. Atomic and molecular interactions between building units are directly corrected with the assembly processes and macroscale structures and properties of the assembled systems. For example, the applications of most functional nanomaterials are involved with multi-scales of length and time with multifunctional mechanisms that are inherently coupled.

There have been many simulation efforts to fully understand the whole event and structures of this multi-scale nature. One of the most studied is combining quantum theory, molecular dynamics, Monte Carlo methods, statistical mechanics, and continuum mechanics within a unified multi-scale framework of model. This in order words bridges the three main different scales (quantum, atomic, and continuum whose fundamental physics are different) that are necessary to address the nanotechnology systems. This is called *multi-scale modeling*. There are two main approaches for this. The sequential (or hierarchical) approach uses the result

obtained at a certain length or time scale as an input for the next level of calculation. The concurrent approach develops a single hybrid method that combines the different levels of length and time scales, usually by combining the atomistic method with the continuum one. For detailed methodologies, refer to Liu et al. (2008).

Multi-scale models become particularly important for systems that bridge the nanoscale structures, properties, and functions with the macroworld, and where whole assembly events are truly on the multi-scale of length and time spanning many orders of magnitudes. These include functional nanomaterials, nanofabricated systems, nanodevices, and nanomechanics. Liu et al. (2008) also provide a comprehensive review of the multi-scale simulations of diverse nanostructures and nanoproperties. For another comprehensive review on multi-scale modeling, see Ghoniem et al. (2003). Vvedensky (2004) presents the details of various different methods and hierarchies between them along with well-selected examples. Ayton et al. (2007) present a multi-scale coarse-graining methodology that uses atomic-level information to build coarse-grained force fields. This method takes advantage of the simplicity and effectiveness of coarse-grained simulation while retaining the structures that were observed in the high-resolution atomic-scale simulation. Mohan and Kopelevich (2008) have developed a multi-scale model for formation of spherical nonionic micelles through combination of coarse-grained molecular dynamics and others, including Brownian dynamics. Their results predict a number of important assembly parameters, including critical micellar concentration (*cmc*), aggregation number, micellar size, and micellar size distribution, with good accuracy.

18.4. CONCLUDING REMARKS

Modeling and simulations for assembly processes and assembled systems have significantly advanced. However, many of the coarse-grained and multi-scale simulation techniques that are critical for self-assembly and nanotechnology systems are system specific. They have to be further fine-tuned and generalized for a wider range of systems. They are currently quite limited in assembly systems whose building units consist of mainly attractive and repulsive segments. To cover the full scope of assembly systems, they eventually need to address all the other segments of assembly building units, including effect of directional force, effect of asymmetric packing, and effect of diverse external forces.

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Epilogue

Informatics for Self-Assembly and Nanotechnology Systems

E.1. BACKGROUND

Over the past few decades, informatic approaches for the analysis of chemical diversities within the chemical space, based on structural or substructural analysis of molecular or genetic materials, have produced tremendous practical progress on many fronts of modern science and technology. Drug discovery, combinatorial science, medicinal chemistry, biochemistry, and molecular biology are among good examples in the spotlight. Largely, this has been possible thanks to ongoing efforts in gathering vast amounts of structural data into various types of structural databases. This structural information is getting connected with the physical, chemical, and biological properties, which are growing exponentially; this makes it possible for us to establish sophisticated structure–property relationships with much improved reliability. Meanwhile, information technology has progressed fast enough to be fused with these databases and matured enough to provide practical algorithms and software to analyze them at the level of molecules and submolecules. Not only do these new disciplines in science provide us great benefits such as functional analysis, high-throughput screening, and fast accessing of existing molecules, but they make it possible for us to predict and test purpose-oriented or custom-derived potential molecules as well. The terms *genomics*, *proteomics*, *bioinformatics*, and *chemoinformatics* come from these new disciplines (Claverie

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and Notredame, 2007; Johnson et al., 2008; Lesk, 2002; Mount, 2001; Pevsner, 2003; Vennila, 2006).

Informatic approaches have great potential and are not limited to the areas mentioned above. They can provide useful insights into broader areas of science and technology by pursuing similar analysis beyond the molecular level. They certainly have the potential to be adopted for nanotechnology. Those areas of informatics are possible mainly because their building units can be analyzed into a manageable number of basic parts and the interactions between them are flexible. Within each building unit in self-assembly and nanotechnology systems, there is a segment (for more about the concept of *segmental analysis*, see Section 1.2) that selectively interacts with a segment from the other building units. The vectorial sum of interactions between the segments determines the assembly of self-assembly and nanotechnology systems. Therefore, once we established the segmental analysis of self-assembly and nanotechnology building units, information technology would be able to provide proper algorithms and software for their combinatorial interactions. This analysis should make it possible for us to analyze the building units into a series of segments that are selective on a specific type of interaction. Then, the informatic tools could provide a systematic analysis and assessment of existing self-assembly and nanotechnology systems. Furthermore, this could provide a practical guide to build new types of self-assembly and nanotechnology systems, possibly with a specific purpose, and to predict their structures and properties.

The recent advances in the fragment-based lead discovery (FBLD) strategy in the area of drug discovery explore the chemical space for potential drug molecules and build target drugs by logically combining small chemical fragments (Oprea and Blaney, 2006; "Piece by Piece," 2008; Rees et al., 2004; Wyss and Eaton, 2007). This can be a good analogy for the segmental analysis of self-assembly and nanotechnology systems. The same is true for the design of a combinatorial fragment library for drug discovery (Martin and Critchlow, 1999). In addition, there have been significant advances in the informatic analysis of the molecular scaffold, which allows us to identify not only overall structural frameworks from vast chemical databases, but detailed structural features including substructural fragments and their networks as well (Bemis and Murcko, 1996; Fialkowski et al., 2005; Karakoc et al., 2006; Lipkus et al., 2008; Willett, 2000). The concept of versatile building blocks for the design of supramolecular coordination assemblies through metal-directed assembly can be another analogy for this (Fujita et al., 2005). The same is true of the concept of secondary building units that have a predetermined directionality for the design and construction of nanoporous metal-organic frameworks through their geometrical packing (Rosi et al., 2005; Yaghi et al., 2003). All these efforts and advances can be viewed as a *bottom-up* approach, as with the bottom-up assembly for nanotechnology systems, toward useful drugs and materials with designed specificity, functionality, and diversity.

The purpose of this epilogue is to propose that the informatics for self-assembly and nanotechnology systems can be a practical tool to address and resolve many of their issues. Self-assembly can bridge nanotechnology and information technology. This book has shown that seemingly complex self-assembly and nanotechnology

systems can indeed be understood with the fragmental analysis–based approach. The term *SANOInformatics* (*S*elf-*A*ssembly and *N*an*o*technology *Informatics*) is here proposed to represent this.

E.2. DEFINITION AND PRINCIPLE

Figure E-1 shows the conceptual flow of SANOInformatics. Self-assembly not only helps assemble nanotechnology systems efficiently, but provides practical tools to control their structures and properties as well. And the concept of force balance (Figure 1-1) makes that this can be done in a systematic manner. Fundamentally, nanotechnology is about how to assemble and manipulate its building units at our will, and the concept of force balance for self-assembly systems can be directly applied to nanotechnology systems. This is based on the fact that self-assembly and nanotechnology systems share (1) almost the same types of building units, (2) the same types of working forces and their interaction ranges, and (3) the same types of assembly mechanisms (Lee, 2008). The concept of force balance thus combines self-assembly systems with nanotechnology systems. The next step is to analyze the building units in a way that is comparable with informatics. This can be done based on the argument, as shown throughout this book, that the building units can be viewed as the sum of the five basic segments. This analysis is valid for atoms, molecules, polymers, colloidal particles, and others, regardless of their origins, including synthetic, biological, and bio-mimetic (Figures 1-3 and 1-5). SANOInformatics then can be established so that the logical combination of the

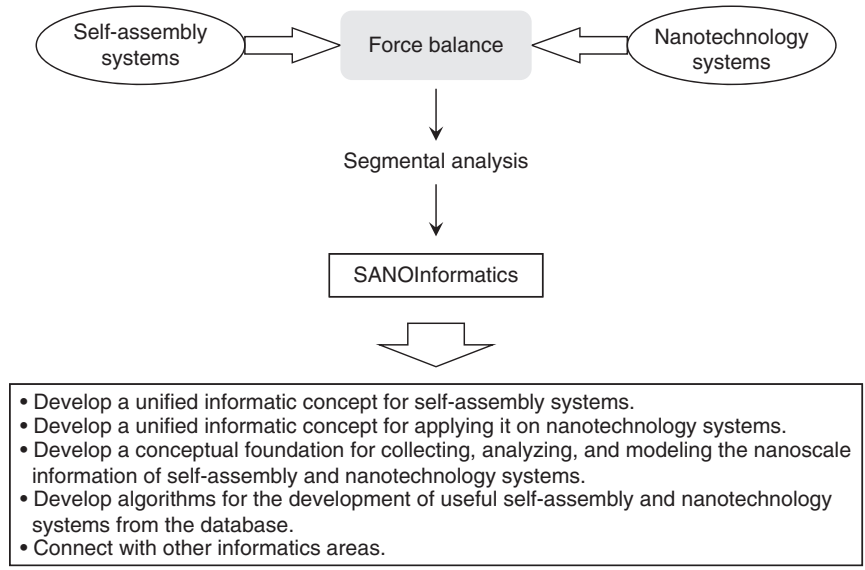
Self-assembly systems
Force balance
Nanotechnology systems
Segmental analysis
SANOInformatics
• Develop a unified informatic concept for self-assembly systems.
• Develop a unified informatic concept for applying it on nanotechnology systems.
• Develop a conceptual foundation for collecting, analyzing, and modeling the nanoscale information of self-assembly and nanotechnology systems.
• Develop algorithms for the development of useful self-assembly and nanotechnology systems from the database.
• Connect with other informatics areas.

Figure E-1. The concept of *SANOInformatics* (*S*elf-*A*ssembly and *N*anotechnology *Informatics*).

five segments and their combinatorial interactions can be performed. This may progress as follows:

1. Develop a unified informatic concept for self-assembly systems.
2. Develop a unified informatic concept for applying it to nanotechnology systems.
3. Develop a conceptual foundation for collecting, analyzing, and modeling nanoscale information of self-assembly and nanotechnology systems.
4. Develop algorithms for the assembly of useful self-assembly and nanotechnology systems from the database.
5. Connect with other informatics areas, which could provide synergistic results.

Nanoinformatics, a much broader concept, is already emerging. This mainly aims at efficient development of nanomanufacturing. Considering the enormity of the range it covers and the inevitable nature of its networking diversities, SANOInformatics would certainly have the opportunity of playing an important part in it.

E.3. STRUCTURE

SANOInformatics is considered to be composed of four structural layers. It begins with the segmental analysis of self-assembly building units (Section 1.2). This yields the corresponding forces that make the second layer (Section 1.2). The third layer is the preceding of self-assembly and the formation of self-assembled systems (Section 1.2). The last layer is the assembly of nanotechnology systems (Sections 2.1, 2.2, and 2.6) and acquisition of nanoelements (Section 2.3). Table E-1 summarizes these four layers of structure and their hierarchical relationships.

Segmental analysis makes up the top-left area of the table. Currently, it can be done qualitatively and, in some cases of amphiphiles, semi-quantitatively. However, there are some informatic tools available. At this point, these are mainly for analysis of molecular skeletons but it might be possible to expand them for more detailed molecular structural analysis. Once all the segments are identified, we can have a clear picture of what types of forces would be involved among them and with how much magnitude. Each segment in the top-left area brings its own unique force. This is the top-right area. Self-assembly makes up the bottom-left area. Up to tertiary assembly processes are shown, but even higher orders of assemblies are possible as long as the force balance allows them. Assembly of nanotechnology systems makes up the bottom-right area. The three previous layers (segmental analysis, force balance, and self-assembly) are required to make reliable decisions for it. The self-assembly building units are now a part of their building units along with fabrication and reactive building units (Section 2.2). Nanotechnology systems should be obtained as long as the force balance between their building units favors their assembly. For many cases, the nanoelements could be estimated with reasonable accuracy by using the knowledge about the building units and the force balance between them.

TABLE E-1. Four layers that compose SANOInformatics. (Abbreviations used in the figures and tables throughout this book are shown as bold letters.)

attractive segment: **A**	attractive force: **AF**
repulsive segment: **R**	repulsive force: **RF**
directional segment: **D**	directional force: **DF**
asymmetric packing segment: **AP**	asymmetric packing process: **APP**
external force–specific functional segment: **EF-F**	external force–induced directional factor: **ED**
self-assembly: **SA**	nanoassembly: **NA**
self-assembled aggregate: **SAA**	nanoassembled system: **NA-S**
self-assembly building unit (primary): **SA-BU**	nanoassembly building unit: **NA-BU**
primary self-assembly process: **P-SA**	fabrication building unit: **F-BU**
primary self-assembled agggregate: **P-SAA**	reactive building unit: **R-BU**
secondary self-assembly building unit: **S-SA-BU**	nanostructural element: **N-SE**
secondary self-assembly process: **S-SA**	nanoproperty element: **N-PE**
secondary self-assembled aggregate: **S-SAA**	nanomechanical element: **N-ME**
tertiary self-assembly building unit: **T-SA-BU**	nanocommunication element: **N-CE**
tertiary self-assembly process: **T-SA**	nanofabrication: **NF**
tertiary self-assembled aggregate: **T-SAA**	

E.4. DEVELOPMENT AND BENEFITS

The realization of practical SANOInformatics might require the following steps:

1. *Acquire data*: It may be a good idea to create an open-access type of collaboration that anyone can join.
2. *Analyze the data* based on the concept of segmental analysis.
3. *Integrate them* into a database.
4. *Analyze the database*: This would be the part that can be learned a lot from other informatics areas.
5. *Provide answers* regarding the analysis and design of self-assembly and nanotechnology systems, and possibly others.

The questions to be addressed on SANOInformatics could include:

1. Would a particular assembly building unit indeed assemble?
2. If so, what type of structure would the assembled system have?
3. What would be the properties of the assembled system?
4. Can the right assembly building units be identified from the structures and properties of the self-assembly system that is at the designing stage?
5. Can the right assembly building units be identified from the structures and nanoelements of the nanotechnology system that is at the designing stage?
6. What would be the properties, structures, and functions of the self-assembly or nanotechnology system that is obtained from the known building units?
7. How about applying this to the fabrication of nanodevices and nanomachines?

A vast amount of knowledge and data on self-assembly systems has already been gathered over the past century, and for nanotechnology systems it continues to accumulate rapidly as well.

E.5. CHALLENGES

SANOInformatics may bring us substantial benefits. Combining the seemingly unrelated issues of self-assembly and nanotechnology systems into one unified framework would help streamline the research processes. At the same time, the challenges ahead include:

1. *How covalent and other strong bonds can be analyzed*: They often become a significant assembly factor in some nanotechnology systems.
2. *How top-down techniques can be incorporated*: They may have a practical role at the manufacturing stage.
3. *How socioscientific issues can be included*: nanotoxicity, nanobioactivity, nanoenvironmental activity, nanogreen activity, and nanomedical activity.

The nanoworld is at the crossroads of the *quantum* and *classical* mechanical worlds. For some systems, both work well. For others, neither work satisfactorily. It might be a good idea to have a new approach.

Finally, it is my hope that someday we will reach the level where we get to control self-assembly and nanoassembly systems at will by performing the fascinating assembly processes examined in this book, just like our children build their own toys out of those little LEGO parts.

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Index

Ab initio method, 432
Actin, bundle, 109
Actuator, self-oscillating gel, 376
Aerosol-OT
  nanoassembly of, directed, 209
  segmental structure of, 197
Aggregate, *see* Self-assembled aggregate
Alkanedithiols
  nanoassembly of, 317
  segmental structure of, 308
Alkanethiols
  nanoassembly of, 289
  nanofabrication of, 343
  segmental structure of, 278, 336
Alkylhexaethylene glycols
  critical micellar concentration of, 67
  segmental structure of, 66
  self-assembly of, 67
Alkylpyridinium bromides
  nanoassembly of, 284
  segmental structure of, 278
Alkylsiloxanes, surface self-assembly of, 86–87, 153
Alkyltrichlorosilanes
  nanoassembly of, 322
  segmental structure of, 308
Alkyltriethoxysilanes
  nanoassembly of, 293
  segmental structure of, 278, 336
Alkyltrimethylammonium bromides
  critical micellar concentration of, 67
  nanoassembly of, 284, 288, 289
  nanofabrication of, 343
  segmental structure of, 278, 308, 336
  self-assembly of, 65, 100
  surface self-assembly of, 83–85
All-at-once nanoassembly, *see* Nanoassembly mode
Ambipolar transport, 326
Amide group, for intrinsic functionality, 264
Amidine, alkyl, 251
Anodic alumina membrane
  for nanodevice, 379, 384
  segmental structure of, 367
Antibody
  nanoassembly of, 322
  segmental structure of, 309
Antimicrobial activity, 329
Assembility, of nanoassembly, 195
Assemblability, of nanoassembly, 195
Assembled system
  simulation of, 429–430
  structural properties for characterization of, 417, 418

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Assembled system (*Continued*)
techniques for characterization of, 400, 401
Assembler building unit, *see* Nanoassembly building unit
Assembler, *see* Self-assembled aggregate
Assembly process
critical phenomena for characterization of, 405–406
simulation of, 429–430
techniques for characterization of, 400, 401
Asymmetric packing process, *see* Force balance theory
Asymmetric packing segment, *see* Segmental analysis
surface-induced asymmetric packing, 149, 154
Atomic force microscopy, 398
Atomistic simulation, 433
Attractive driving force, 4
Attractive force, *see* Force balance theory
Attractive segment, *see* Segmental analysis
Axial dislocation, for surface nanoassembly, 290
Azo-benzene-based building unit
for intrinsic functionality, 265
for nanodevice, 379
self-assembly of, 233, 251

Bacterial actin MreB, for nanodevice, 382
Bacterial flagellar motor, 388
Bacterial flagellar protofilament, 387
Bactericidal activity, 329
Belousov-Zhabotinsky (BZ) reaction, 315, 329
Bicelle, 90
Binary colloidal crystal, *see* Colloidal crystal
Biocomparability, as intrinsic functionality, 271
Bioinformatics, 258
Biological self-assembled aggregate, *see* Self-assembled aggregate
Biomineral, 186
Biotin-avidin interaction, 320–321
Biotoxicity, 322
Birefringence, 322
Birefringent colloidal crystal, *see* Colloidal crystal
Bis(ethylhexyl) sodium sulfosuccinate, *see* Aerosol-OT
Bis(triethoxysilyl) ethane
nanoassembly of, directed, 210
segmental structure of, 198
Black film, 90
BRAHMS, 435
Branched rod, 138
Brownian dynamics, 435
Building block, 3
Building unit, 3
Bundled helical chain, 157
β-sheet, 158

Cadmium telluride
nanoassembly of, 319
segmental structure of, 309
Calcium carbonate
nanoassembly of, 326
segmental structure of, 309
Cantilever tip, AFM, 317
Capillary torque, 395
Carbon nanotube
for nanodevice, 375, 383, 387
nanoassembly of, 178
potential applications of, 301
properties of, 301
segmental structure of, 166, 366
single-walled, surface silylated, 166
Casimir force, for self-assembly, 105, 249–250
Catalysis, as intrinsic functionality, 271
Catalytic reaction, for self-assembly, 236
Catenane
for nanodevice, 379
segmental structure of, 367
Cell, 109
Cellulose fiber, 106
Centrifugal force, for nanoassembly, 211, 217
Cetyltrimethylammonium bromide, nanoassembly of, 319
Cetyltrimethylammonium chloride
nanoassembly of, 282
nanoassembly of, directed, 210, 211
segmental structure of, 197
Chain-like, 138
Chaotic, 138
Chemical database, 441
Chemical space, 11, 258, 442
Chemical vapor deposition, 220
Chemo-mechanical planarization, 346
Chirality, *see* Self-assembled aggregate
Chloroauric acid
nanoassembly of, 288
segmental structure of, 279
Cholic acid-based amphiphile, 251
Cholic acid-based steroid cyclophane, 251
Cholic acid-based tetraaminocalixarene, 251
Chromo-capillary effect, 328
Circular-type, 137
Cis-trans isomerization, for nanodevice, 379
Coarse-grained simulation, 433–434
Coil, 158
Collagen
fiber, 106, 109
nanoassembly of, 178, 184
segmental structure of, 165

Colloidal cluster, 90
Colloidal crystal, 106, 169, 185, 200
  binary, 173, 205–206
  birefringent, 204
  for nanoassembly, 284
  with controlled number/symmetry, 209
Colloidal force, *see* Intermolecular/colloidal force
Colloidal monolayer, 90
Colloidal wire, *see* Polystyrene colloidal particle
Columnar, 138
Concentric circular, 157
Conductivity, 408
Continuum simulation, 436
Controller building unit, *see* Nanoassembly building unit
Controller, *see* Self-assembled aggregate
Coordination bond, 7
Coumarin 460, segmental structure of, 365
Covalent bond, 7
Critical aggregation number (*can*), 16, 408, 411
Critical assembly parameter, 414
Critical micellar concentration (*cmc*), 16, 67, 405, 408, 411
Critical phenomena, 405
  for characterization of assembly process, 405–407
  physical properties for characterization of, 406
Critical point, 5, 405
Critical state, *see* Critical point
Crystal-like, 138
Cyano pentyl biphenyl (5CB)
  nanoassembly of, 322
  segmental structure of, 308
Cyanoporphyrin, 351–352
Cyclodextrin-based dimer, 251
Cyclodextrin-based organogel, 252

Decanedithiol, nanoassembly of, 317, 319
Dendrimer, amphiphilic, 251
Dendritic, 138
Density functional theory, 432
Depletion agent, 103
Diindenoperylene
  nanoassembly of, 326
  segmental structure of, 308
Dimeric, 138
Dimethyl propanoic acid, zirconium salt
  nanoassembly of, 169
  segmental structure of, 166
Dipalmitoyl phosphatidylcholine
  chirality of, 146
  hierarchy of, 146
  segmental structure of, 118, 133
  self-assembly of, 118
Dipalmitoyl phosphatidylethanolamine
  nanoassembly of, forced, 201
  segmental structure of, 197
Dip-coating, 220
Dip-pen lithography, 343
Directed nanoassembly, *see* Nanoassembly
Directional force, *see* Force balance theory
Directionality, of nanoassembly, 195
Directional segment, *see* Segmental analysis
Disk, 137
Dissipative particle dynamics, 434
Disulfide-based building unit, self-assembly of, 236, 251
DLVO theory, 430
DNA
  as directional segment of colloid, 126, 129
  double helix, 109
  for intrinsic functionality, 268
  for nanodevice, 384
  nanostructure, 300
  segmental structure of, 368
Dodecyldimethylamine oxide, self-assembly of, 240, 251
Dodecyldimethyl(hydroxyethyl)ammonium
  chirality of, 151
  hierarchy of, 151
  segmental structure of, 118, 133
  self-assembly of, 118
Dodecyltrimethylammonium bromide
  chirality of, 146, 151
  hierarchy of, 146, 151
  multi-step self-assembly of, 97, 100, 133
  nanoassembly of, 178, 184
  segmental structure of, 66
  self-assembly of, 67
  surface self-assembly of, 83–85
Double emulsion, 90
Double helix, 138, 158
Drag-reducing, as intrinsic functionality, 271
Drug discovery, 258
Dual-hierarchy, 146
Dumbbell, colloidal, 129–130
Dynein, 388

Elaidic acid, 122
  molecular packing at membrane, 123–124
Elastic model, 431
Electric field, for nanoassembly, 206, 219, 249
Electrochemical reaction, for self-assembly, 238
Electrodeposition, 220
Electron cascade, 319
Electronic simulation, 432
Electron transport, 320
Electrospinning, 220
Element force, 36, 362

Element motion, *see* Nanomechanics
Ellipsoid, 137
Emulsion, water-in-oil, for nanoassembly, 209
Endosome, 109
Environmental susceptibility, as intrinsic functionality, 271
Enzyme, 106
Epitaxial adlayer, 90
Epitaxial matching, 221
Etching, 346, 348, 352
Evaporation, for nanoassembly, 200, 205, 220
External force (signal), 194
  critical window for nanoassembly, 218
External force-induced directional factor, *see* Segmental analysis, Force balance theory
External force specific functional segment, *see* Segmental analysis
External signal (force), 228
External signal-responsive functionality, 261
External signal-responsive nanomaterial, *see* Nanomaterial

F_1-adenosine triphosphate synthase (F_1-ATPase)
  for nanodevice, 372, 372–373
  segmental structure of, 368
Ferroceniumyl alkanethiol
  nanoassembly of, 326
  segmental structure of, 308
Ferroceniumyl-based building unit, self-assembly of, 238
Ferrocenyl-based building unit, self-assembly of, 238, 251
Ferromagnetic nanorod, self-assembly of, 247, 251
Fiber, 106
Fibril-in-fibril, 157
Fibrous, 138
Field effect transistor (FET), 319, 354
Finger-like, 137
Fluidic device, 354
Fluorescein, segmental structure of, 365
Fluorocarbon, for intrinsic functionality, 264
Foam, 90
Foam-like, 137
Folded-chain, 138
Folded helical chain, 157
Force balance theory, 4–6; *see also* Segmental analysis
  asymmetric packing process, 36
  at surface, 83–85
  attractive force, 4
  directional force, 4
  external force-induced directional factor, 12, 220
  for SANOInformatics, 443
  functional force, 4
  point of initial force balance, 16
  repulsive force, 4
Force-distance curve, 396, 398, 399
Forced nanoassembly, *see* Nanoassembly
Force field, 433
Fractal, 138
Fracture resistance, 326
Frictional adhesion, 299
Fullerene
  nanoassembly of, 322
  nanofabrication of, 343
  segmental structure of, 308, 336
Fullerene-in-carbon nanotube, 157
Fullerene-wheeled compound
  for nanodevice, 372
  segmental structure of, 365
Functional force, *see* Force balance theory
Functionalizer building unit, *see* Nanoassembly building unit
Functionalizer, *see* Self-assembled aggregate

Gallium arsenide
  nanoassembly of, 322, 326
  segmental structure of, 309
Gel, 106
Gelation, as intrinsic functionality, 271
Geometrical model, 431
Germanium-silicon, alloy, nanoparticle, 288
Germanium vapor
  nanoassembly of, 293
  segmental structure of, 279
Glass
  nanoassembly of, 326
  segmental structure of, 309
Gluconate-based building units
  for intrinsic functionality, 264
  segmental structure of, 78, 118, 133
  self-assembly of, 118
Glucopyranosylamine octadecanoyl
  segmental structure of, 119
  self-assembly of, 119
Glucopyranosyloxy phenyl octadecanamide
  segmental structure of, 119
  self-assembly of, 119
Gold nanohexagon
  segmental structure of, 126
  self-assembly of, 126, 135
Gold nanoparticle
  decanethiol-protected, 166
  design of, 288–289
  for nanodevice, 381, 384
  nanoassembly of, 169, 173, 174, 181, 182, 288–289, 322
  nanofabrication of, 341

patterned semiconductor device, 169
segmental structure of, 126, 166, 309, 336, 366
self-assembly of, 126, 135
Gold-silver, nanorod, 289
Gold surface
nanoassembly of, 319, 326
nanofabrication of, 343
segmental structure of, 309, 336
Gold vapor
nanoassembly of, 169, 183
segmental structure of, 166
Graphite, highly oriented pyrolytic (HOPG)
for nanoassembly, 293
segmental structure of, 279
Green chemistry, 161
Green nanoscience, 162
Green nanotechnology, 162
Guide motion, *see* element motion

H-aggregate, 106
Hamaker constant, 74
Helical chain, 158
Helical rod, 138
Helical tube, 158
Helix (α-), 138
Hemimicelle, 86, 90
Herringbone reconstruction, 221
Heterogeneous nanoassembly, *see* Nanoassembly route
Hetero-strip, 138
Hexagonal prism morphology, for intrinsic functionality, 268
Hierarchical chirality, 146
Hierarchically patterned surface, 293, 302
Hierarchical nanoassembly, *see* Nanoassembly mode
Hierarchical self-assembly, *see* Self-assembly
Hierarchy, *see* Self-assembled aggregate
Higher-order self-assembled aggregate, *see* Self-assembled aggregate
Higher-order self-assembly building unit, *see* Self-assembly building unit
Higher-order self-assembly, *see* Self-assembly
HKUST-1, *see* Metal-organic framework
Hollow sphere, 137
Hollow tube, 138
Homogeneous nanoassembly, *see* Nanoassembly route
Hydrogelator, low molecular weight, 266–267
Hygroscopicity, 322

Immunoglobulin, *see* Antibody
Indentation, 341
Indium tin oxide (ITO)
nanoassembly of, 326
nanofabrication of, 348
segmental structure of, 309
Indium vapor
nanoassembly of, 326
segmental structure of, 310
Informatics, 441–442
Inorganic light-emitting diode (ILED), 350
Interface, for nanoassembly, 293; *see also* Surface
Intermolecular/colloidal force, 395–396
collection of, 397
implication for self-assembly, 31
measurement of, 396–399
techniques for measurement of, 400
Intramolecular force, *see* Intermolecular/colloidal force
Intrinsic functionality, of nanomaterial, *see* Nanomaterial
Inverse colloidal crystal, 173, 185
Ion exchanger, 319
Ionic bond, 7
IRMOF series, *see* Metal-organic framework
Iron nanoparticle, self-assembly of, 76–77
Iron oxide nanoparticle, for intrinsic functionality, 268
Iron oxide nanorod, self-assembly of, 247
Island-type, 137
Isotherm, 431

J-aggregate, 106
Janus balance, 73
Janus particle, 73, 289

Keggin polyoxometalate
nanoassembly of, directed/forced, 205, 216
segmental structure of, 197
Kinesin
for nanodevice, 380, 381
segmental structure of, 368

Langmuir-Blodgett deposition, 220
Langmuir-Blodgett monolayer, 90
Langmuir-Blodgett multilayer, 106, 293
Langmuir monolayer, 90, 293
Langmuir-Shafer deposition, 220
Lap-on-a-chip device, 354
Layer-by-layer film, 106, 220
Lead sulfide, nanowire, 290
LEGO block, 3, 30–31, 446
and nanoassembly, 34–35, 59–60
and nanotechnology system, 34–35, 59–60
and self-assembly, 30–31
and self-assembly system, 3–4, 30–31
Liesegang rings, 221
Liposome, 90

Liquid crystal, 157
Lithography, 346, 348
Lustrin A-based adhesive protein mixture
  nanoassembly of, 326
  segmental structure of, 309
Lysosome, 109

Macroemulsion, 90
Macroscopic device, 53
Macroscopic machine, 53
Magnetic field, for nanoassembly, 210, 247
Manipulative assembly, 52
MARTINI, 436
MCM series, *see* Mesoporous material
Mean-field theory, 433
Mechanical assembly, 52
Mechanical force, for nanoassembly, 205, 216
Mechanochemical alloying, 346
Memory storage device, 355
Mercaptoalkane trimethoxysilanes
  nanofabrication of, 341
  segmental structure of, 336
Mercaptoalkanoic acid
  for nanodevice, 376
  segmental structure of, 365
Mesochannel, 210
Mesophase, 106
Mesoporous material, 186, 300, 349
Mesosome, 109
Metal-organic chemical vapor deposition, 169, 220
Metal-organic framework (MOF), 188, 300, 337, 348, 349
Methylthiol, 154
Micellar solubilization, 270
Micelle, 90
  for nanoassembly, 210, 211, 282, 284
  multi-compartment, 267
Microcapsule, 137
Micro-contact printing, 348
Microelectromechanical system (MEMS), 354
Microemulsion, 90
  for nanoassembly, 282, 288
Microgel, for nanodevice, 384
Micropump, catalytic, 387
Microtubule, 109
  for nanodevice, 380, 381
  segmental structure of, 368
MIL series, *see* Metal-organic framework
Mitochondrial membrane, 106
Modeling, of assembly system, 429–430
MOF series, *see* Metal-organic framework
Molecular automaton, 388
Molecular dynamics simulation, 433
Molecular geometry, on self-assembly, 233, 236, 238
Molecular motor, 379, 387
Molecular rotor, altitudinal, 377–378
Monte Carlo simulation, 433
Montmorillonite
  nanoassembly of, 319
  segmental structure of, 309
Motor protein, 368
Multimeric, 138
Multiple rings, 138
Multiple sheets, 138, 157
Multiple stack, 138
Multi-scale simulation, 436–437
Multi-step self-assembly, *see* Self-assembly
Myosin, 388

Nanoassembled system, 52
Nanoassembly, 35, 52
  chiral (asymmetric), 290
  directed, 194
  forced, 194
  functional, 49
  general rules of, 43, 46
  hierarchy with self-assembly and nanofabrication, 51–54
  multi-step, hierarchical, 49
  point of initial force balance, 43, 46, 48
  reference system for, 46
  universal assembly diagram of, 49
  with multiple building units, 162
Nanoassembly building unit, 37, 54
  as assembler, 322
  as controller, 326
  as frame, 319, 322, 326
  as functionalizer, 319
  building unit structure for nanoassembly, 42
  fabrication building unit, 36, 38
  force balance for, 35
  functional surface, 56–57
  ligand-protected nanoparticle, 54–56
  rational combination of, 36
  reactive building unit, 36, 40
  reactive precursor, 57
  reducing agent, 58
  segmental analysis for, 36
  self-assembly building unit, 6, 23, 36
  substrate, 57–58
Nanoassembly mode, 36, 163–164
  all-at-once mode, 163
  hierarchical mode, 163
  sequential mode, 163
  successive mode, 163
Nanoassembly route, 36, 45
  forced route, 192

heterogeneous route, 164
homogeneous route, 163
spontaneous route, 192
Nanoassembly system, 52–53
Nanocar, 372
Nanocargo, 381
Nanochannel, 211, 220, 367
Nanocomposite, 157, 173, 174, 178, 185, 284, 288, 302
Nanoconfinement, 300
Nanodevice, *see* Nanomechanics
Nanoelectromechanical system (NEMS), 354
Nanoelement, 36, 48
definition of, 41
nanocommunication element, 42
nanomechanical element, 42
nanoproperty element, 41
nanostructural element, 41
Nanoelevator, 381
Nanofabricated system, 52
applications of, 354–355
definition of, 52, 333–334
fabrication of, 341, 343, 346, 348
functional modification of, 353
key nanoproperties for, 354–355
key nanostructures for, 354–355
Nanofabrication, 52
bottom-up approach, 335, 341, 343
bottom-up/top-down hybrid approach, 335, 341, 348
bulk materials for, 337, 353
definition of, 52, 333–334
hierarchy with self-assembly and nanoassembly, 51–54
top-down approach, 335, 341, 346
top-down techniques for, 337, 352
unit fabrication, 335, 341
Nanogate, 376
Nanogel, polyethylene glycol-modified, 176–177
Nanoinformatics, 444
Nanointegrated system, 52, 341
Nanoisland, 221, 290, 293
Nanolayered film, 293
Nano-logic gate, 383
Nanomachine, *see* Nanomechanics
Nanomaterial
external signal-responsive, characterization of, 426
external signal-responsive, collection of, 254
external signal-responsive, definition of, 227–228
with intrinsic functionality, collection of, 271
with intrinsic functionality, definition of, 257
Nanomechanical movement, *see* Nanomechanics
Nanomechanical sensor, 384
Nanomechanics
definition of, 359–360
element motions for, 361–362
external signals for, 387–388
mechano-motions for, 387–388
nanodevice, 52, 359
nanodevice, different types, 363, 387–388
nanomachine, 52, 359
nanosystems for, 387–388
unit operation, 359
working mechanisms, 363, 372, 375, 376, 379, 381, 384, 385
Nanomotor, 372, 375, 387
Nanooscillator, 372, 383
Nanoparticle
alternative-type, 289
binary, 289
core-shell, 268
gold-silica core-shell, 289
Janus-type, 289
tethered, 130
Nanoparticle chain-in-nanofiber, 157
Nanoparticle-in-nanoshell, 157
Nanopatterned film, 288, 293
Nanopiston, 379
Nanopore, dual-porosity silica, 178
Nanoporous film, 293
Nanoporous material, 186, 300
Nanoproperty, 305
collective type, 314, 315, 324
cooperative type, 314
individual type, 314, 320–321
nanosystem for, 328, 329, 330
potential applications of, 328, 329, 330
Nanoreactor, 277, 282, 287
Nanoribbon, 157, 158
Nanorod
alternative-type, 289
binary, 289
gold, 288
tethered, 269–270
Nanoshuttle, 379
Nanospring, 379, 384
Nanostructural element, 275; *see also* Nanoelement
of nanofilm, 296
of nanoparticle, 292
of nanopore, 286
Nanostructural parameter, 314
Nanostructure, 275
common names of, 299
hierarchically ordered silica, 178
nanofilm-based, 276, 282, 297

Nanostructure (*Continued*)
nanoparticle-based, 276, 282, 288–289, 297
nanopore-based, 276, 282, 284, 297
potential applications of, 300, 301, 302
properties of, 300, 301, 302
Nanoswitch, 375, 376
Nanotechnology, 33
Nanotechnology system, 33
in relation with self-assembly system, 60
nanoscale system, 33
nanosystem, 33
Nanothermosensor, 384
Nanotoxicity, 324
Nanowire, lead sulfide, 290
Nanoworld, 446
Naphthyridinyl urea derivative, 252
Networked helical chain, 157
Nickel nanorod, surface modified
for nanodevice, 372
segmental structure of, 366
Niosome, 90
Nuclear envelop, 106

Oblate, *see* Spheroid
Octadecenoic acid (9-*cis*), *see* Oleic acid
Octadecenoic acid (9-*trans*), *see* Elaidic acid
Oleic acid
molecular packing at membrane, 123–124
segmental structure of, 119
self-assembly of, 119
Oligoheterocyclic-type building unit, 251
Oligopyridine, 134
One-by-one assembly, 343, 344, 344–345
Organic-inorganic hybrid material, 185
Organic light emitting diode (OLED), 322
Organosilica, nanostructured, 210
Oxidation, localized, 319
Oxybispyridine-based complex, 252

Palmitoyl oleoyl phosphatidylcholine
nanoassembly of, 293
segmental structure of, 278
Patchy particle model, 434–435
Peptide amphiphile, 266
Peroxisome, 109
Phenylacetylene oligomer, 252
pH, for self-assembly, 240, 246
Photocatalytic activity, 330
Photochemical effect, 330
Photochromic effect, 330
Photoelectric effect, 330
Photonic band gap, 169, 200
Photolithography, 337
Photovoltaic device, 355
Planar sheet, 137
Plasma-enhanced chemical vapor deposition, 220
Plasma membrane, 106
Platinum
mesoporous, 201–202
nanoassembly of, 319
segmental structure of, 309
Point of force balance, 408, 411; *see also* Self-assembly
Poly(acrylic acid), self-assembly of, 246, 251
Polydimethylsiloxane (PDMS) stamp, 348
Poly(ethyleneimine)
nanoassembly of, 174
segmental structure of, 165
Polyethylene oxide, for intrinsic functionality, 264
Polyethylene oxide, with thiol end group
nanoassembly of, 319
segmental structure of, 308
Polyimide-based building unit, 251
Poly(methyl methacrylate) colloidal particle
nanoassembly of, directed, 209
nanoassembly of, directed/forced, 208
nanoassembly of, forced, 200, 215
segmental structure of, 197
surface alkylated, 198
Poly(*N*-isopropylacrylamide)
for intrinsic functionality, 268
for nanodevice, 384
segmental structure of, 366
self-assembly of, 244, 251
Polyoxometalate, *see* Keggin polyoxometalate
Poly(phenylacetylene)-based building unit, 251
Poly(pyrrole)-based nanorod, self-assembly of, 248
Polystyrene colloidal particle
colloidal wire of, 206, 207
nanoassembly of, 169, 173, 182, 284
nanoassembly of, directed/forced, 206
nanoassembly of, forced, 200
nanofabrication of, 343
segmental structure of, 165, 197, 279, 336
Porphyrins, 155–156
Primary aggregate, *see* Primary self-assembled aggregate
Primary self-assembled aggregate, *see* Self-assembled aggregate
Primary self-assembly building unit, *see* Self-assembly building unit
Primary self-assembly, *see* Self-assembly
Prolate, *see* Spheroid
Protein, 106, 252
Protein adsorption, 319
Protein immobilization, 320
Protrusion, for nanoassembly, 201

Pull motion, *see* Element motion
Push motion, *see* Element motion
Pyramidal-like, *see* Multiple stack
Pyrene-β-cyclodextrin, self-assembly of, 241–242

Quantum dot, 301
Quantum simulation, 432

Reaction rate, as intrinsic functionality, 271
Repulsive force, *see* Force balance theory
Repulsive opposition force, 4
Repulsive segment, *see* Segmental analysis
Reverse mesophase, 106
Reverse micelle, 90
Reverse segmental analysis, *see* Segmental analysis
Rhodamine B, segmental structure of, 366
Ribbon, 138
Ribosome, 109
Ring-type, 137
RNA, 109
Rod, 137
Rotaxane
  for nanodevice, 379, 381, 384
  segmental structure of, 367

SANOInformatics, 443
SBA series, *see* Mesoporous material
Schizophrenic block copolymer, 252
Secondary self-assembled aggregate, *see* Self-assembled aggregate
Secondary self-assembly building unit, *see* Self-assembly building unit
Secondary self-assembly, *see* Self-assembly
Segmental analysis, 7; *see also* Force balance theory
  additional segment, 11–12
  asymmetric packing segment, 12
  attractive segment, 7
  directional segment, 7
  external force-induced directional factor, 12, 220
  external force-specific functional segment, 12
  for nanoassembly building unit, 36
  for SANOInformatics, 443
  for self-assembly building unit, 7–15
  fundamental segment, 7
  general rules between segments, 16
  of surfactant molecules, 66
  rational combination of segments, 7, 11, 12
  repulsive segment, 7
  reverse segmental analysis, 159
Self-assembled aggregate
  as assembler, 307, 317
  as controller, 307, 317
  as functionalizer, 307, 317
  biological, 107–108
  chirality, characterization of, 424
  chirality of, 141–142
  external force effect, characterization of, 425
  hierarchy, characterization of, 424
  hierarchy of, 141–142
  higher-order, 105–107, 113–115, 137–139
  higher-order, characterization of, 423
  primary, 90, 93, 106, 109, 112–113, 136–137
  primary, characterization of, 420
  secondary, 93, 96, 97
  tertiary, 93, 96, 97
Self-assembled monolayer, 90, 293, 302
Self-assembled system, 52
Self-assembly
  assembly coordination, 6
  assembly profile, 6
  biological, 19
  bio-mimetic, 19, 78
  capability, 64
  capability, characterization of, 408
  catalytic reaction-responsive, 236
  chiral, 19
  dynamic, kinetic, 6
  electrochemical responsive, 238
  external force effect, characterization of, 425
  functional, 19
  general rules of, 18
  hierarchy with nanoassembly and, 51–54
  higher-order, 93, 97
  light-responsive, 233
  magnetic field-responsive, 247
  multi-step, characterization of, 411
  multi-step, hierarchical, 94, 100, 103
  of ionic surfactant, 69–70
  parameters of, 414
  pH-responsive, 240, 246
  point of initial force balance, 16, 18, 20
  primary, 93, 97
  reference system for, 18, 20
  secondary, 93, 97
  static, thermodynamic, 6
  surface, 81
  tertiary, 93, 97
  thermo-responsive, 244
  universal assembly diagram of, 20
Self-assembly building unit, 6, 23
  asymmetrically packing, 28
  basic, 23–26
  directionally assembling, 26–28, 78
  functional, 28–30
  higher-order, 93, 97
  primary, 63, 93, 97

Self-assembly building unit (*Continued*)
reference, 18, 20
secondary, 97
tertiary, 97
Self-assembly system, in relation with nanotechnology system, 60
Self-cleaning window, 326
Self-consistent field theory, *see* Mean-field theory
Self-propelled nanodevice, 319
Self-reassembly, 351–352
Semiconductor nanorod, self-assembly of, 248–249, 251
Semi-empirical calculation, 432
Semimicelle, 88, 90, 151
Separation, as intrinsic functionality, 271
Sequential nanoassembly, *see* Nanoassembly mode
Silica
as nanocomposite, 173, 284
dual-pore, 178, 184
for surface self-assembly, 151
inverse opal, 173
mesoporous hollow sphere, 343
nanofilm, 282, 284
nanohelix, 175
nanoparticle, 282
nanopore, 282, 284
Silica nanoparticle
multi-step self-assembly of, 102–104
nanoassembly of, 322
segmental structure of, 72, 279, 309
self-assembly of, 71–73, 75–77, 252
Silica, nanoporous
for nanoassembly, 288, 293, 322
for nanodevice, 376
segmental structure of, 309, 367
Silicate anion
nanoassembly of, 173, 178
segmental structure of, 166
Silicon
as substrate for nanoassembly, 169, 183, 284, 293
nanoassembly of, 288
nanofabrication of, 341
segmental structure of, 279, 309, 336
surface oxidized, 279
Silicon nanogroove
nanoassembly of, 322
segmental structure of, 309
Silicon nanorod
nanoassembly of, 319
segmental structure of, 309
Silver nanoparticle
dodecanethiol-protected, 198
nanoassembly of, 317
nanoassembly of, directed/forced, 205
segmental structure of, 198, 309
Silver vapor
nanoassembly of, 289
segmental structure of, 279, 337
Simulation, of assembly system, 429–430
Smart material, 253
Smart surface, 253
Socio-scientific issue, 446
Sodium adamantane carboxylate, as external-signal, 241–242
Sodium alkyl sulfate
nanoassembly of, 319, 322
segmental structure of, 308
Sol-gel film, 106
Sol-gel reaction, 173
Son block cream, 319
Sphere, 137
Spheroid, 137
Spin-coating, 220
Spiral, 158
Spiral surface defect, 221
Spontaneous nanoassembly, *see* Nanoassembly route
Step edge, 221
Stilbene amide cyclodextrin, 251
Strain-relief pattern, 221
Strip, 137
Successive nanoassembly, *see* Nanoassembly mode
Superhydrophobic surface, 293, 302
Superparamagnetic nanorod, 251
Surface, alloying, 288
Surface critical micellar concentration (*cmc*), 84, 85
Surface dislocation, 221
Surface-enhanced Raman scattering (SERS) substrate, 205, 317
Surface forces apparatus, 399
Surface force, *see* Intermolecular/colloidal force
Surface, for nanoassembly
liquid, 293
solid, 211
Surface micelle, 90
for nanoassembly, 284
Surface mismatch, 221
Surface plasmonic device, 169, 317
Surface self-assembly, *see* Self-assembly
lying-down mode, 85, 88
up-right mode, 85, 88
Surface stress, 221
Surface symmetry, 221

Surface tension, 408
Surface well, 287
Symmetry-broken layer, 158

Temperature, for self-assembly, 244
Template, 277, 282, 284, 286
Tertiary self-assembled aggregate, *see* Self-assembled aggregate
Tertiary self-assembly building unit, *see* Self-assembly building unit
Tertiary self-assembly, *see* Self-assembly
Tethered nanoparticle, *see* Nanoparticle
Tetraethyl orthosilicate
  nanoassembly of, 282, 284, 288–289, 293
  segmental structure of, 279
Tetramethyl orthosilicate, segmental structure of, 337
Thermodynamic model, 430
Titania
  nanoassembly of, 319, 326
  nanostructured film, 211, 217
  segmental structure of, 309
Titanium tetrachloride
  nanoassembly of, directed, 211, 217
  segmental analysis of, 198
Top-down technique, *see* Nanofabrication
Transport, as intrinsic functionality, 271
Tree-like, *see* Branched rod
Triethoxysilyl alkanoic acid
  for nanodevice, 376
  segmental structure of, 365
Trimeric, 138
Triple-hierarchy, 146
Tubular, 138
Tungstomanganatesilicate, *see* Keggin polyoxometalate
Twisted rod, 138

Ultrasound
  effect on intermolecular forces, 203
  for nanoassembly, 200
Ultraviolet block, 319
Ultraviolet/visible light, for self-assembly, 233
Unit fabrication, *see* Nanofabrication
Unit operation, *see* Nanomechanics

Vacuole, 109
Vapor deposited film, 90, 106, 185, 220
Vectorial sum, 229
Vesicle, 90, 201
Vesicle-in-nanotube, 157
Vesicle-in-vesicle, 157
Vesosome, 106
Vicinal surface, 221
Virus, 109
Viscosity, 411

Zeolite, 187, 300
ZIF series, *see* Metal-organic framework
Zinc phthalocyanine
  nanofabrication of, 348
  segmental structure of, 336
Zinc sulfide, nanohelix, 175
Zirconia, thin film device, 169